Exhibit A

IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

BRIDGESTONE SPORTS CO., LTD., and BRIDGESTONE GOLF, INC. Plaintiff, v. ACUSHNET COMPANY, Defendant.	C. A. No. 05-132 (JJF)

DECLARATION OF JOSEPH LAVELLE

I, Joseph Lavelle, counsel for the Acushnet Company in the above-referenced matter, declare as follows:

1. On Monday November 13, 2006, I traveled to Acushnet's headquarters in Fairhaven, Massachusetts to meet with its General Counsel, Joseph Nauman to discuss the status of this case. Also present at this meeting were Troy Lester, Acushnet's Chief Patent Counsel, and Robin Adelstein, outside litigation counsel.

2. At this meeting, one of the subjects I discussed was my request that Acushnet's in-house personnel conduct additional prior art searches for prior art relating to the '791 patent.

3. The next day, on November 14, I had a telephone conference with Mr. Nauman and three Acushnet engineers (Jeff Dalton, Bill Morgan, and Mike Sullivan) to discuss the parameters of these additional prior art searches.

4. Over the next two weeks, Acushnet's engineers conducted prior art searches. I began receiving the results of these searches during the week of November 27, and learned of new prior art patents at that time. These included U.S. Patent Nos. 5,779,563; 5,967,908;

5,872,185; 6,267,694; and 6,174,247. Neither I nor anyone at Howrey to my knowledge knew of this prior art before about the last week of November.

5. I consider these new patents to be highly material to the invalidity of the '791 patent. It is my belief that one or more of the prior art references anticipates the asserted claims of the '791 patent. It is also my belief that the Altus Newing Massy golf ball manufactured by Bridgestone in the 1990s is highly material to and anticipates the '707 patent, as recent testing has indicated. Acushnet would be severely prejudiced if it could not rely on this art at trial.

6. Consequently, I directed the lawyers at Howrey to include these new prior art references in Acushnet's supplemental interrogatory answers. These were served by agreement between the parties on December 18, 2006.

I declare under penalty of perjury under the laws of the United States of America that the foregoing is true and correct.

Dated: January 3, 2007

/s/ Joseph Lavelle

Joseph Lavelle

Exhibit B

US005779563A

United States Patent [19]

Yamagishi et al.

[11] **Patent Number: 5,779,563**

[45] **Date of Patent: Jul. 14, 1998**

[54] **MULTI-PIECE SOLID GOLF BALL**

[75] Inventors: **Hisashi Yamagishi; Yasushi Ichikawa; Atsushi Nakamura**, all of Chichibu, Japan

[73] Assignee: **Bridgestone Sports Co., Ltd.**, Tokyo, Japan

[21] Appl. No.: **796,454**

[22] Filed: **Feb. 10, 1997**

Related U.S. Application Data

[60] Provisional application No. 60/017,271 May 13, 1996.

[30] **Foreign Application Priority Data**

Feb. 9, 1996 [JP] Japan 8-048137

[51] **Int. Cl.**[6] **A63B 37/06**; A63B 37/12

[52] **U.S. Cl.** **473/371**; 473/373; 473/384

[58] **Field of Search** 473/374, 373, 473/384, 372, 377, 378

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,714,253	12/1987	Nakahara et al.	473/374 X
5,002,281	3/1991	Nakahara et al.	473/374 X
5,497,996	3/1996	Cadorniga	473/378 X
5,553,852	9/1996	Higuchi et al.	473/378 X
5,601,503	2/1997	Yamagishi et al.	473/384

Primary Examiner—George J. Marlo
Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC

[57] **ABSTRACT**

A multi-piece solid golf ball comprises a solid core and a cover of at least two layers enclosing the core and having a number of dimples in cover outer layer surface. The solid core is formed of a rubber base and has a specific gravity of at least 1.00. The cover is formed of a thermoplastic resin and the cover outer layer has a greater specific gravity than the core or a cover inner layer. The golf ball has an inertia moment (M) within the range given by the following expression: $M_{DL} \leqq M \leqq M_{UL}$ wherein M_{UL}=0.08D+84.8 and M_{DL}=0.08D+77.8 wherein D is a Shore D hardness of the cover, the dimples occupy at least 60% of the ball surface, and V_0 is in the range of 0.4 to 0.65. The ball is improved in flight distance, controllability, roll and straight travel upon putting.

5 Claims, 2 Drawing Sheets

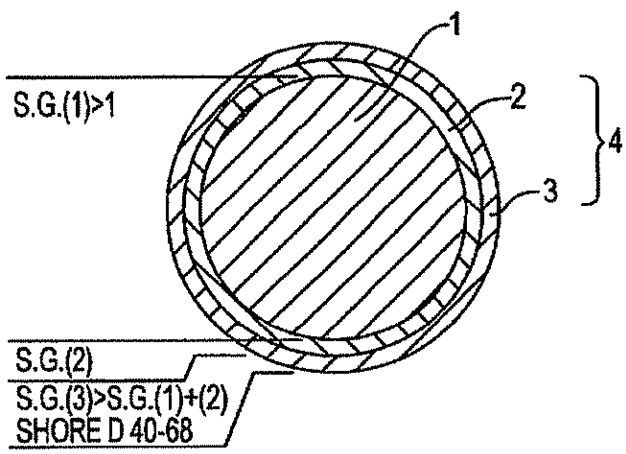


FIG. 1

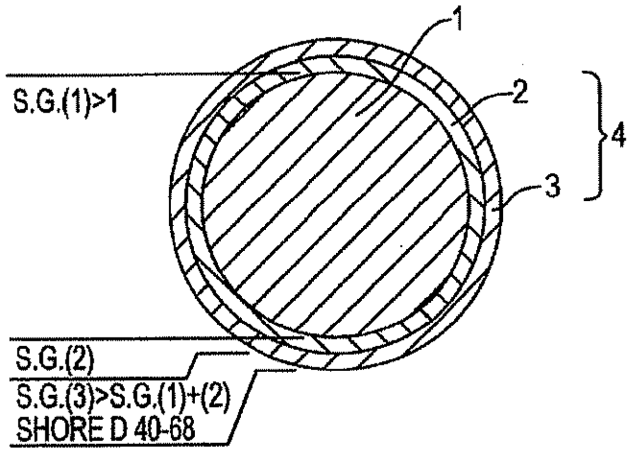


FIG. 2

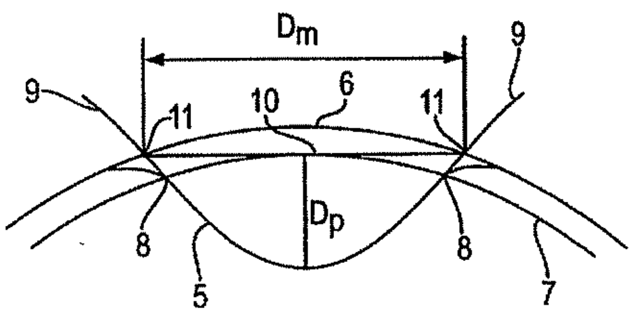


FIG. 3

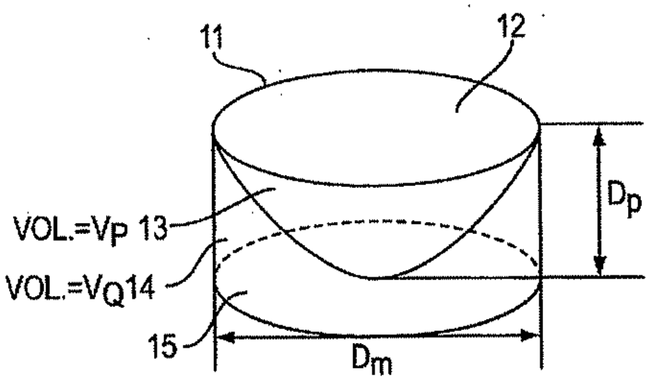
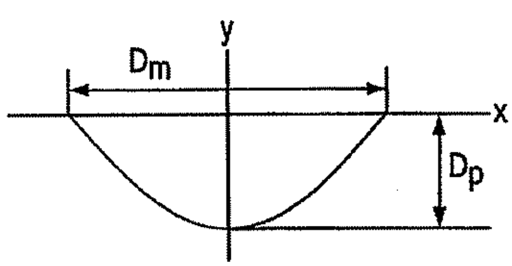


FIG. 4



MULTI-PIECE SOLID GOLF BALL

CROSS REFERENCE TO RELATED APPLICATIONS

This application is an application filed under 35 U.S.C. § 111(a) claiming benefit pursuant to 35 U.S.C. § 119(e) (i) of the filing date of the Provisional application 60/017,271 filed May 13, 1996, pursuant to 35 U.S.C. § 111(b).

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a multi-piece solid golf ball which is improved in flying distance, controllability, roll and straight travel upon putting as well as restitution and durability.

2. Prior Art

Many covers of golf balls used in the art are composed mainly of ionomer resins and have a specific gravity of about 0.96. In order that solid golf balls be usable in competitions, they must meet the requirements prescribed in the Rules of Golf (R&A) and be manufactured to a weight of not greater than 45.93 grams and a diameter of not less than 42.67 mm. Therefore, golf balls obtained using cover stocks composed mainly of ionomer resins will have an inertia moment within a certain range.

The inertia moment of a golf ball largely affects the flight trajectory, flight distance, and control of the ball. In general, an increased inertia moment permits the golf ball to follow an elongated trajectory because the spin attenuation rate of the golf ball in flight is reduced so that the spin is maintained when the ball descends past the maximum altitude. Also when hit on the green with a putter, the ball will go straight and roll well. For these reasons, several proposals have been made on golf balls to impart a greater inertia moment thereto.

For example, Japanese Pat. application Kokai (JP-A) No. 277,312/1994 proposes a solid golf ball which is made from an ionomer resin base having titanium white and barium sulfate blended therein so that the ball may have a greater inertia moment.

This proposal, however, suffers from the problems that the golf ball can be scraped and chafed upon iron shots because the cover formed thereon contains much fillers such as titanium white and barium sulfate and that the ball cannot travel a satisfactory distance because the large filler content deteriorates the restitution of the cover.

SUMMARY OF THE INVENTION

An object of the invention is to provide a multi-piece solid golf ball having a cover which has an optimum inertia moment for a certain hardness of a cover outermost layer and an optimum dimple pattern so that the ball is improved in flying distance, controllability, straight travel and roll upon putting as well as durability.

Making extensive investigations to attain the above object, the inventors have found that a multi-piece solid golf ball having a cover of at least two layers is improved in flying distance, controllability, roll and straight travel upon putting on the green as well as restitution and cover durability against iron shots when the core is formed to a specific gravity of 1.00 or higher using a rubber base material, the cover outer layer is formed to a greater specific gravity than the core, the ball has an inertia moment (M) within the range given by the following expression:

$$M_{DL} \leqq M \leqq M_{UL}$$

wherein M_{UL}=0.08D+84.8 and M_{DL}=0.08D+77.8 wherein D is a Shore D hardness of a thermoplastic resin of which the cover outer layer is made, that is, an inertia moment is selected in accordance with a cover outer layer hardness, dimples occupy at least 60% of the ball surface, and V_0 which is the ratio of the volume of the dimple space below a plane circumscribed by the dimple edge to the volume of a cylinder whose bottom is the plane and whose height is the maximum depth of the dimple from the bottom is in the range of 0.4 to 0.65, and preferably, the core hardness, an index (Dst) of overall dimple surface area given by the following expression:

$$Dst = \frac{n \sum_{k=1}^{n} |(Dmk^2 + Dpk^2) \times V_0k \times Nk|}{4R^2}$$

wherein R is a ball radius, Nk is the number of dimples k, and V_0 is as defined above, and the cover outer layer hardness are optimized, and advantageously in this embodiment, the cover outer layer is formed of a thermoplastic polyurethane elastomer.

Accordingly, the present invention provides a multi-piece solid golf ball comprising a solid core and a cover of at least two layers enclosing the core and having a number of dimples in the surface of a cover outer layer, wherein

said solid core is formed of a rubber base and has a specific gravity of at least 1.00,

said cover is formed of a thermoplastic resin and the cover outer layer has a greater specific gravity than the core and a cover inner layer,

the golf ball has an inertia moment (M) within the range given by the following expression:

$$M_{DL} \leqq M \leqq M_{UL}$$

wherein M_{UL}=0.08D+84.8 and M_{DL}=0.08D+77.8 wherein D is a Shore D hardness of the cover,

the dimples occupy at least 60% of the ball surface,

and V_0 which is the ratio of the volume of the dimple space below a plane circumscribed by the dimple edge to the volume of a cylinder whose bottom is the plane and whose height is the maximum depth of the dimple from the bottom is in the range of 0.4 to 0.65.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a golf ball according to one embodiment of the invention;

FIG. 2 is a schematic view (cross-sectional view) of a dimple illustrating how to calculate V_0.

FIG. 3 is a perspective view of the same dimple.

FIG. 4 is a cross-sectional view of the same dimple.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in further detail. As shown in FIG. 1, the multi-piece solid golf ball of the invention comprises a solid core 1 formed of a rubber base and a cover 4 on the core consisting of two layers, an inner layer 2 and an outer 3. The cover 4 consists of two or more layers.

The solid core 1 should have a specific gravity of at least 1.00, preferably 1.02 to 1.18, more preferably 1.06 to 1.15.

The solid core 1 used herein may be made of well-known materials and formed by conventional techniques while

properly adjusting vulcanizing conditions and formulation. The core formulation used herein may contain a base rubber, crosslinking agent, co-crosslinking agent, and inert filler. The base rubber which can be used herein is natural rubber and/or synthetic rubber used in conventional solid golf balls. It is preferred in the practice of the invention to use 1,4-polybutadiene having at least 40% of cis-structure. The polybutadiene may be blended with natural rubber, polyisoprene rubber, styrene-butadiene rubber or the like, if desired.

The crosslinking agent which can be used herein is an organic peroxide such as dicumyl peroxide and di-t-butyl peroxide, especially dicumyl peroxide. The amount of the crosslinking agent blended is preferably 0.5 to 1.8 parts by weight, especially 0.8 to 1.5 parts by weight per 100 parts by weight of the base rubber.

The co-crosslinking agent is not critical. Examples are metal salts of unsaturated fatty acids, inter alia, zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms (e.g., acrylic acid and methacrylic acid), with zinc acrylate being especially preferred. The amount of the co-crosslinking agent blended is 10 to 40 parts by weight, preferably 15 to 35 parts by weight per 100 parts by weight of the base rubber.

Examples of the inert filler include zinc oxide, barium sulfate, silica, calcium carbonate, and zinc carbonate, with zinc oxide being often used. The amount of the filler blended is not particularly limited because the amount largely varies with the specific gravity of the core and cover, the weight prescription of the ball, and other factors. Usually, the amount of filler is preferably 5 to 25 parts by weight, more preferably 7 to 20 parts by weight per 100 parts by weight of the base rubber.

A core-forming composition is prepared by kneading the above-mentioned components in a conventional mixer such as a Banbury mixer and roll mill, and it is compression or injection molded in a core mold. The molding is then cured by heating at a sufficient temperature for the crosslinking agent and co-crosslinking agent to function (for example, a temperature of about 130° to 170° C. for a combination of dicumyl peroxide as the crosslinking agent and zinc acrylate as the co-crosslinking agent), obtaining a core.

By a proper choice of the type and amount of compounding materials, especially crosslinking agent and co-crosslinking agent and vulcanizing conditions, a core having a desired hardness (as expressed by a distortion under a load of 100 kg) can be obtained. Herein, the core is preferably formed to yield a distortion under a load of 100 kg of 2.0 to 5.0 mm, more preferably 3.0 to 4.8 mm. With a distortion falling within this range, sufficient restitution, pleasant hitting feel, and improved scraping resistance are achievable.

It is noted that the solid core 1 preferably has a diameter of 25 to 41 mm, especially 30 to 40 mm and a weight of 20 to 40 grams, especially 23 to 39.5 grams.

Next, the cover 4 enclosing the above-mentioned solid core 1 consists of two or more layers and is preferably of a two-layer structure of cover inner and outer layers 2 and 3.

The cover outer layer 3 is formed to a greater specific gravity than the core 1 and the cover inner layer 2, thereby achieving a high inertia moment and producing a golf ball having excellent flight stability and go-straight stability upon putting. In contrast, the object of the invention is not achievable if the cover outer layer's specific gravity is lower than the specific gravity of the core and cover inner layer. The cover outer layer's specific gravity is properly selected in accordance with the specific gravity of the core and cover

inner layer although it is preferred that the cover outer layer is formed to a specific gravity of at least 1.10, especially 1.10 to 1.25 and the difference of specific gravity between the cover outer layer and the core is 0.01 to 0.15.

Also the cover outer layer hardness is not critical although the cover outer layer is preferably formed to a Shore D hardness of 40 to 68, more preferably 43 to 65. A Shore D hardness of less than 40 would lead to low restitution whereas a Shore D hardness of more than 68 would blunt the hitting feel.

The cover outer layer stock used herein is not critical insofar as the cover outer layer is formed to a greater specific gravity than the solid core and cover inner layer. The cover outer layer may be formed of conventional cover stocks, preferably thermoplastic resins. The thermoplastic resins used herein include thermoplastic polyurethane elastomers, ionomer resins, polyester elastomers, polyamide elastomers, propylene-butadiene copolymers, 1,2-polybutadiene, and styrene-butadiene copolymers. These resins may be used alone or in admixture of two or more. It is preferred in the practice of the invention to use thermoplastic polyurethane elastomers as a base, for example, PANDEX T-7890 and PANDEX T-1198 (trade name, by Dai-Nihon Ink Chemical Industry K.K.). To satisfy the cover's specific gravity defined above, various fillers such as barium sulfate, titanium oxide and magnesium stearate may be blended in the thermoplastic resin.

Desirably the cover inner layer has a specific gravity of 0.9 to 1.2 and the cover outer layer has a specific gravity of at least 1.10 as mentioned above. It is also preferred that the cover outer layer has a highest specific gravity among the core, cover inner and outer layers.

The gage of the cover inner and outer layers is arbitrary although it is preferred that the cover inner layer has a gage of 0.3 to 2.5 mm and the cover outer layer has a gage of 0.3 to 2.5 mm.

Understandably, the golf ball may be manufactured by conventional methods. That is, the golf ball can be obtained by preforming a pair of half cups of single or multi-layers from a cover stock, and encasing the solid core in the cover by compression molding or the like to thereby form a cover of two or more layers. Alternatively, the cover may be formed by injection molding.

Also the golf ball of the invention has an inertia moment (M) in proportion to the cover outer layer hardness (Shore D hardness) within the range given by the following expression:

$$M_{DL} \leq M \leq M_{UL}$$

wherein M_{UL}=0.08D+84.8 and M_{DL}=0.08D+77.8 wherein D is a Shore D hardness of the cover outer layer.

More specifically, we have found that the inertia moment should fall in an optimum range correlated to the cover hardness. The inertia moment should be greater when the cover is hard, but need not be greater as required for the hard cover when the cover is soft. This is because a ball with a soft cover provides a greater frictional force upon impact and receives more spin whereas a ball with a hard cover provides a less frictional force and receives less spin. A hard cover ball launched at a low spin rate will attenuate its spin fast and stall on falling if the inertia moment is low. Inversely, a soft cover ball launched at a high spin rate will experience less spin attenuation if the inertia moment is too high, so that the ball will rather climb up during flight due to more spin than necessity. In either case, the ball tends to travel a shorter distance.

Consequently, the inertia moment of a ball should fall within the above-defined range from the standpoint of imparting excellent characteristics to a ball. An inertia moment below the lower limit of the above-defined range would lead to a stalling trajectory whereas an inertia moment above the upper limit of the above-defined range would lead to a rather climb-up trajectory. In either case, the carry is reduced.

The inertia moment (M) within the above-defined range is determined by the following equation.

$$M=\frac{\pi}{580000}\{(r_1-r_2)xD_1^5+(r_2-r_3)xD_2^5+r_3D_3^5\}$$

r_1, D_1: core specific gravity, diameter

r_2, D_2: intermediate layer specific gravity, diameter

r_3, D_3: cover specific gravity, ball diameter

Like conventional golf balls, the solid golf ball of the invention is formed with a multiplicity of dimples in the surface. The golf ball of the invention is formed with dimples such that, provided that the golf ball is a sphere defining a phantom spherical surface, the proportion of the surface area of the phantom spherical surface delimited by the edge of respective dimples relative to the overall surface area of the phantom spherical surface, that is the percent occupation of the ball surface by the dimples is at least 60%, preferably 60 to 80%. With a lower dimple occupation, the inertia moment in flight has less of the above-mentioned effect. The number of dimples is preferably 350 to 500, more preferably 360 to 460. The arrangement of dimples may be as in conventional golf balls. There may be two or more types of dimples which are different in diameter and/or depth. It is preferred that the dimples have a diameter of 2.5 to 4.3 mm and a depth of 0.14 to 0.25 mm.

Moreover, the dimples are formed such that V_0 is 0.40 to 0.65, especially 0.43 to 0.60 wherein V_0 is the ratio of the volume of the dimple space below a plane circumscribed by the dimple edge to the volume of a cylinder whose bottom is the plane and whose height is the maximum depth of the dimple from the bottom. If V_0 exceeds 0.65, there is a likelihood that the ball climb up and stall, covering a shorter distance. If V_0 is below 0.40, the trajectory would tend to descend.

Now the shape of dimples is described in further detail. In the event that the planar shape of a dimple is circular, as shown in FIG. 2, a phantom sphere 2 having the ball diameter and another phantom sphere 3 having a diameter smaller by 0.16 mm than the ball diameter are drawn in conjunction with a dimple 1. The circumference of the other sphere 3 intersects with the dimple 1 at a point 4. A tangent 5 at intersection 4 intersects with the phantom sphere 2 at a point 6 while a series of intersections 6 define a dimple edge 7. The dimple edge 7 is so defined for the reason that otherwise, the exact position of the dimple edge cannot be determined because the actual edge of the dimple 1 is rounded. The dimple edge 7 circumscribes a plane 8 (having a diameter Dm). Then as shown in FIGS. 3 and 4, the dimple space 9 located below the plane 8 has a volume Vp. A cylinder 10 whose bottom is the plane 8 and whose height is the maximum depth Dp of the dimple from the bottom or circular plane 8 has a volume Vq. The ratio V_0 of the dimple space volume Vp to the cylinder volume Vq is calculated.

$$Vp=\int_0^{\frac{Dm}{2}}2\pi xydx$$

$$Vq=\frac{\pi Dm^2Dp}{4}$$

$$V_0=\frac{Vp}{Vq}$$

In the event that the planar shape of a dimple is not circular, the maximum diameter or length of a dimple is determined, the plane projected shape of the dimple is assumed to be a circle having a diameter equal to this maximum diameter or length, and V_0 is calculated as above based on this assumption.

Furthermore, the golf ball of the invention wherein the number of types of dimples formed in the ball surface is n and the respective types of dimples have a diameter Dmk, a maximum depth Dpk, and a number Nk wherein k=1, 2, 3, . . . , n prefers that an index Dst of overall dimple surface area given by the following equation is at least 4.0, more preferably 4.0 to 7.0.

$$Dst=\frac{\pi\sum_{k=1}^{n}\{(Dmk^2+Dpk^2)xV_0kxNk\}}{4R^2}$$

Note that R is a ball radius, V_0 is as defined above, and Nk is the number of dimples k. The index Dst of overall dimple surface area is useful in optimizing various dimple parameters so as to allow the golf ball of the invention having the above-mentioned solid core and cover to travel a further distance. When the index Dst of overall dimple surface area is equal to or greater than 4.0, the aerodynamics (flying distance and flight-in-wind) of the golf ball are further enhanced.

The multi-piece solid golf ball of the invention is improved in flying distance, controllability, roll and straight travel upon putting and is less susceptible to scraping upon iron shots.

EXAMPLE

Examples of the present invention are given below together with Comparative Examples by way of illustration and not by way of limitation.

Examples and Comparative Examples

By kneading a core stock as shown in Table 1 and vulcanizing it in a mold at 160° C. for about 18 minutes, there were prepared solid cores having a weight, diameter, specific gravity and distortion under a load of 100 kg as shown in Table 4.

Golf balls were then obtained by separately kneading an outer cover stock as shown in Table 2 and an inner cover stock as shown in Table 4 and forming them into half cups, successively placing the half cups around the core, and effecting compression molding while forming dimples on the outer layer surface in a pattern as shown in Table 3. The parameters and performance properties of the resulting golf balls were examined, with the results shown in Table 4.

The properties of the golf balls reported in Table 4 were evaluated by the following tests.

Inertia Moment

The diameter of the respective members was an average of diameters measured at arbitrary 5 points. As to weight, the

ball was disintegrated into the respective members, which were measured for weight. The net weight and volume were calculated therefrom and the specific gravity of the respective members was calculated therefrom. The inertia moment was determined by substituting these values in the following equation.

$$M=\frac{\pi}{580000}\left[(r_1-r_2)xD_1^5+(r_2-r_3)xD_2^5+r_3D_3^5\right]$$

r_1, D_1: core specific gravity, diameter

r_2, D_2: intermediate layer specific gravity, diameter

r_3, D_3: cover specific gravity, ball diameter

Flying Distance

Using a hitting machine manufactured by True Temper Co., the ball was actually hit at a head speed (HS) of 45 m/sec. with a driver to measure a carry and a total distance.

Scrape Resistance

Using a swing robot, the ball was hit at arbitrary two positions, once at each position, at a head speed of 38 m/sec. with a sand wedge (SW). The two hit zones were observed to evaluate according to the following criteria.

O: good Δ: ordinary X: poor

Continuous Durability

Using a flywheel hitting machine, the ball was repeatedly hit at a head speed of 38 m/sec. In terms of the number of hits counted until the ball was broken, evaluation was made according to the following criteria.

O: good Δ: ordinary X: poor

Feeling

The ball was actually hit by three professional golfers with a head speed of 45 to 50 m/sec. Evaluation was made according to the following criteria.

O: soft Δ: ordinary X: hard

TABLE 1

Core formulation (pbw)	E1	E2	E3	E4	CE1
Cis-1,4-polybutadiene	100	100	100	100	90
Polyisoprene	—	—	—	—	10
Zinc acrylate	32.5	32.5	29.5	25.0	27.0

TABLE 1-continued

Core formulation (pbw)	E1	E2	E3	E4	CE1
Zinc oxide	9.2	10.5	8.5	16.2	14.6
Dicumyl peroxide	1.2	1.2	1.2	1.2	1.2
Zinc salt of pentachlorothiophenol	0.2	0.2	0.2	0.2	—

TABLE 2

	Outer cover type		
Formulation (pbw)	A	B	C
PANDEX T-7890*1	100		
PANDEX T-1198*2		100	
HIMILAN 1706*3			50
SURLYN 8120*4			50
$BaSO_4$ (s.g. 4.47)			20
TiO_2 (s.g. 4.3)	5.3	5.3	5.3
Magnesium stearate	0.5	0.5	0.5
Specific gravity	1.175	1.21	1.13

*1Dai-Nihon Ink Chemical Industry K.K., adipate polyol, thermoplastic polyurethane

*2Dai-Nihon Ink Chemical Industry K.K., adipate polyol, thermoplastic polyurethane

*3Mitsui-duPont K.K., Zn ionomer

*4E. I. duPont, Na soft ionomer

TABLE 3

Dimple type	Diameter (mm)	Depth (mm)	V_o	Number	Surface occupation (%)	Dst
I	4.100	0.210	0.500	54	68.7	4.137
	3.850	0.210	0.500	174		
	3.400	0.210	0.500	132		
II	4.150	0.210	0.480	54	70.3	4.061
	3.850	0.210	0.480	174		
	3.500	0.210	0.480	132		
III	3.650	0.195	0.390	150	62.7	1.961
	3.500	0.195	0.390	210		

TABLE 4

		E1	E2	E3	E4	CE1	CE2	CE3
Core	Weight	25.44	29.02	26.19	27.10	33.53	25.44	14.69
	Diameter	35.50	37.00	36.00	36.00	38.70	35.50	27.70
	Distortion under 100 kg load	2.20	2.20	2.60	3.30	2.50	2.20	4.00
	Volume	23.43	26.52	24.43	24.43	30.35	23.43	11.13
	Specific gravity	1.086	1.094	1.072	1.109	1.105	1.086	1.320
Inner cover	Type *5	a	a	a	b	—	a	a
	Weight (g)	33.20	35.90	32.84	32.84	—	33.20	34.52
	Diameter (mm)	38.75	39.70	38.75	38.75	—	38.75	38.30
	Volume	7.04	6.24	6.04	6.04	—	7.04	18.29
	Specific gravity (calcd.)	1.102	1.102	1.102	0.950	—	1.102	1.102
	Net weight	7.76	6.88	6.65	5.74	—	7.76	20.15
	Gage	1.63	1.35	1.38	1.38	—	1.63	5.30

TABLE 4-continued

Outer cover	Type	A	A	B	B	C	A	D
	Volume	10.30	8.00	10.30	10.30	10.42	10.30	11.35
	Net weight (g)	12.10	9.40	12.46	12.46	11.77	12.10	10.78
	Specific gravity	1.175	1.175	1.210	1.210	1.130	1.175	0.950
	Gage (mm)	1.98	1.50	1.98	1.98	2.00	1.98	2.10
	Shore D hardness	45	45	53	53	55	45	65
Ball	Weight (g)	45.30	45.30	45.30	45.30	45.30	45.30	45.30
	Diameter (mm)	42.70	42.70	42.70	42.70	42.70	42.70	42.70
Inertia moment		85.2	85.0	85.8	84.8	84.5	85.2	80.6
	M_{UL}	88.4	88.4	89.0	89.0	89.2	88.4	90.0
	M_{DL}	81.4	81.4	82.0	82.0	82.2	81.4	83.0
Dimple type		I	II	I	II	I	III	I
Flying distance	Carry (m)	184.5	185.2	185.7	185.5	180.3	177.0	183.0
@HS40	Total (m)	198.6	199.0	200.0	200.5	195.7	191.5	197.5
Scrape resistance		○	○	○	○	X	○	○
Continuous durability		○	○	○	○	Δ	○	Δ
Feeling		○	○	○	○	Δ	○	○

*5 Inner cover type	a	b
HYTREL 4047	100	
HIMILAN 1706		50
HIMILAN 1605		50

We claim:

1. A multi-piece solid golf ball comprising a solid core and a cover of at least two layers enclosing the core and having a number of dimples in the surface of a cover outer layer, wherein

said solid core is formed of a rubber base and has a specific gravity of at least 1.00,

said cover is formed of a thermoplastic resin and the cover outer layer has a greater specific gravity than the core and a cover inner layer,

the golf ball has an inertia moment (M) within the range given by the following expression:

$$M_{DL} \leqq M \leqq M_{UL}$$

wherein M_{UL}=0.08D+84.8 and M_{DL}=0.08D+77.8 wherein D is a Shore D hardness of the cover,

the dimples occupy at least 60% of the ball surface,

and V_0 which is the ratio of the volume of the dimple space below a plane circumscribed by the dimple edge to the volume of a cylinder whose bottom is the plane and whose height is the maximum depth of the dimple from the bottom is in the range of 0.4 to 0.65.

2. The multi-piece solid golf ball of claim 1 wherein said solid core experiences a distortion of 2.0 to 5.0 mm under a load of 100 kg.

3. The multi-piece solid golf ball of claim 1 wherein n types of dimples are formed in the cover, the respective types of dimples have a diameter Dmk, a maximum depth of the dimples is Dpk, and a number of the dimples is Nk wherein k=1, 2, 3, ... n, and

an index (Dst) of overall dimple surface area given by the following expression:

$$Dst = \frac{\pi \sum_{k=1}^{n} \{(Dmk^2 + Dpk^2) \times V_0 k \times Nk\}}{4R^2}$$

wherein R is a ball radius, Nk is the number of dimples k, and V_0 is as defined above is at least 4.0.

4. The multi-piece solid golf ball of claim 1 wherein said cover outer layer has a Shore D hardness of 40 to 68.

5. The multi-piece solid golf ball of claim 1 wherein said cover outer layer is formed of a polyurethane elastomer.

* * * * *

Exhibit C

US005967908A

United States Patent [19]

Yamagishi et al.

[11] Patent Number: 5,967,908

[45] Date of Patent: Oct. 19, 1999

[54] GOLF BALL

[75] Inventors: Hisashi Yamagishi; Hiroshi Higuchi; Yasushi Ichikawa; Junji Hayashi, all of Chichibu, Japan

[73] Assignee: Bridgestone Sports Co., Ltd., Tokyo, Japan

[21] Appl. No.: 09/069,280

[22] Filed: Apr. 29, 1998

[30] Foreign Application Priority Data

May 9, 1997 [JP] Japan 9-136101

[51] Int. Cl.[6] A63B 37/06; A63B 37/12; A63B 37/14

[52] U.S. Cl. 473/373; 473/374; 473/384

[58] Field of Search 473/373, 374, 473/375, 376, 378, 383, 384

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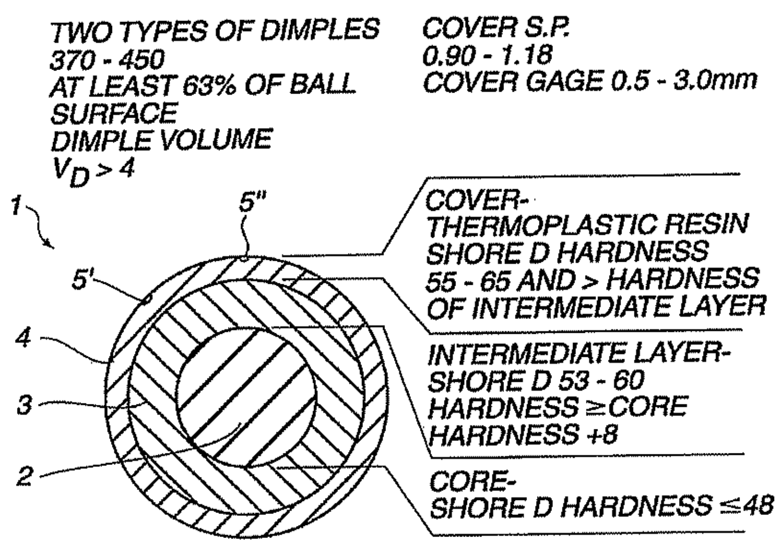
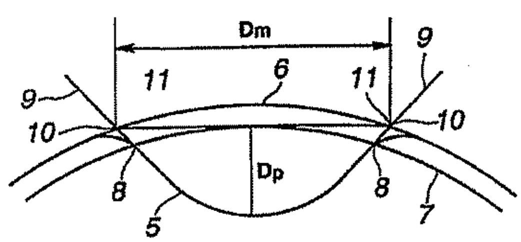
Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC

[57] ABSTRACT

A golf ball includes a solid core, an intermediate layer, and a cover having dimples formed therein. The core has a Shore D hardness at the surface of 30–48, the intermediate layer has a Shore D hardness of 53–60, and the cover has a higher Shore D hardness of 55–65. In the cover, 370 to 450 dimples of at least two types having different diameters and/or depths are distributed so as to cover at least 63% of the ball surface. The index Dst of the overall dimple surface area is at least 4. The golf ball provides significantly improved flight distance and a good feel by virtue of a good balance in hardness and optimized dimple characteristics.

3 Claims, 3 Drawing Sheets





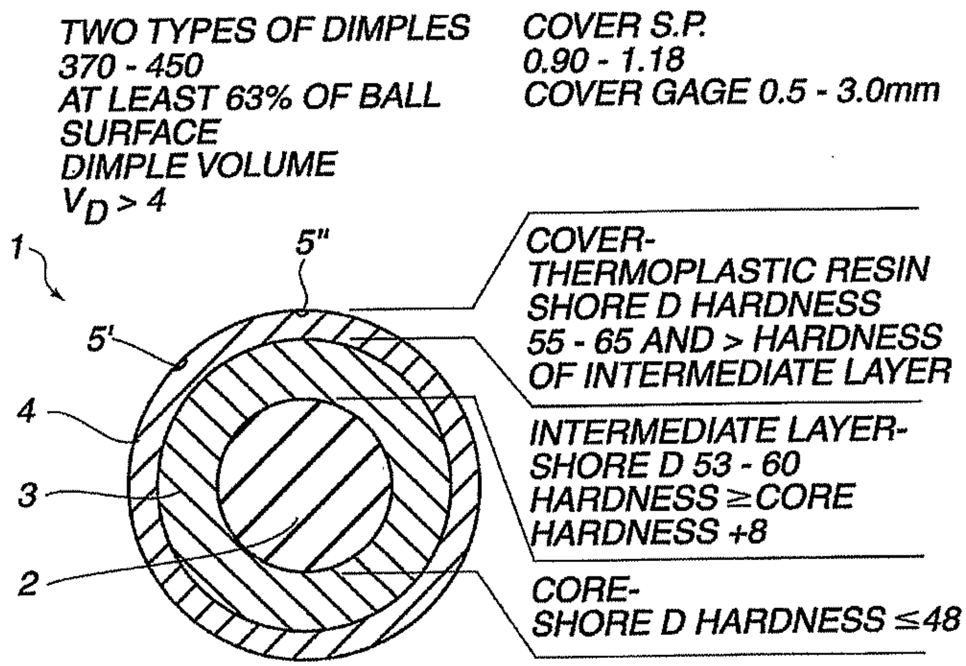

TWO TYPES OF DIMPLES
370 - 450
AT LEAST 63% OF BALL SURFACE
DIMPLE VOLUME
VD > 4
COVER S.P.
0.90 - 1.18
COVER GAGE 0.5 - 3.0mm
1
5"
5'
4
3
2
COVER-
THERMOPLASTIC RESIN
SHORE D HARDNESS
55 - 65 AND > HARDNESS
OF INTERMEDIATE LAYER
INTERMEDIATE LAYER-
SHORE D 53 - 60
HARDNESS ≥ CORE
HARDNESS +8
CORE-
SHORE D HARDNESS ≤ 48

FIG. 1

FIG.2

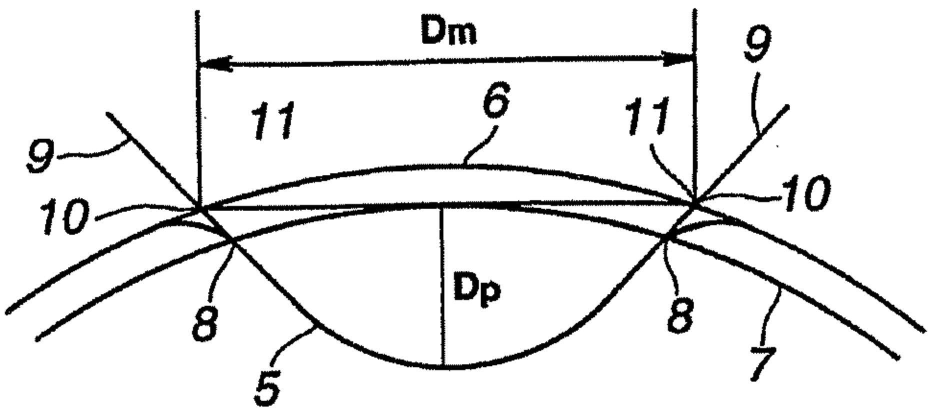


FIG.3

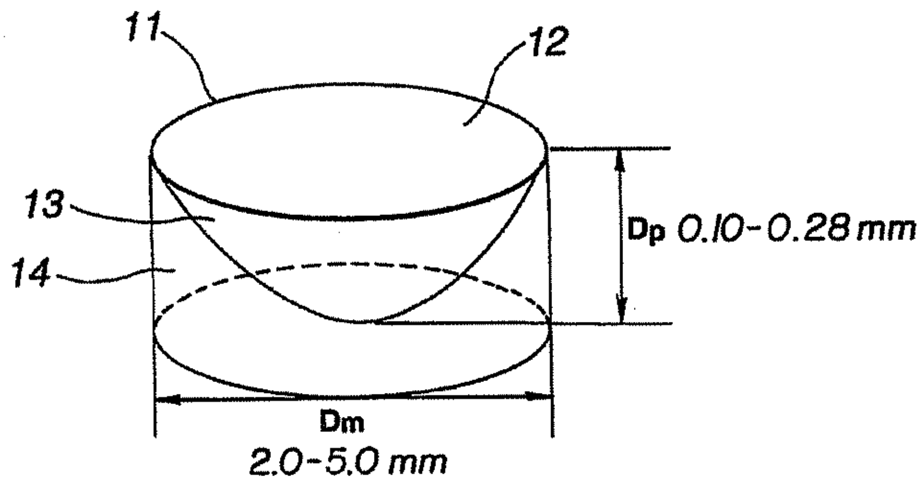
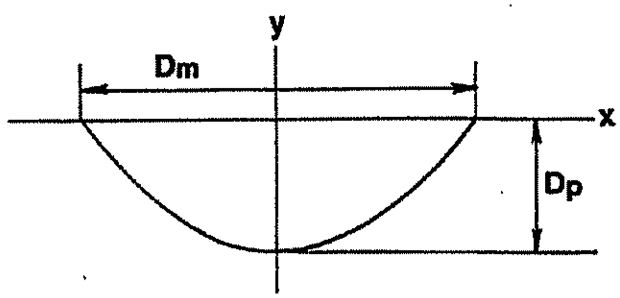


FIG.4



GOLF BALL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a golf ball comprising a solid core, an intermediate layer, and a cover having a multiplicity of dimples formed on its surface. More particularly, the invention relates to a golf ball having an optimum balance in hardness between the core, the intermediate layer and the cover, and having suitable dimple characteristics, thus presenting both a good feel when hit with a club and improved flight performance regardless of the club head speed.

2. Prior Art

With the rise in the golfing population in recent years, the attributes that golfers look for in a golf ball have become more diverse and individualized. The desire is especially strong for golf balls having greater flight distance and a better feel. This has led to numerous investigations on ball construction, dimple parameters and so forth.

For instance, golf balls having a variety of constructions are available today on the market, but the majority of commercial golf balls are either two-piece solid golf balls made of a rubber-based core and a cover composed of ionomer resin or the like, or thread-wound golf balls composed of a thread-wound core obtained by winding rubber thread about a solid or liquid center, and a cover formed over the core.

Most golfers of ordinary skill use two-piece golf balls because of their excellent flight performance and durability. However, these balls have a very hard feel, in addition to which the rapid separation of the ball from the head of the club results in poor control. For this reason, many professional golfers and skilled amateurs prefer using thread-wound balls to two-piece solid balls. Yet, although thread-wound golf balls have a superior feel and control, their distance and durability fall short of those for two-piece balls.

Thus, two-piece golf balls and thread-wound golf balls today provide mutually opposing features, and so golfers select which type of ball to use based on their level of skill and personal preference.

This situation has prompted efforts to achieve the feel of a thread-wound ball in a solid golf ball, as a result of which a number of soft two-piece solid golf balls have been proposed. A soft core is used to obtain such soft two-piece balls, but making the core softer lowers the resilience of the golf ball and compromises flight performance and durability. As a result, not only do these balls lack the excellent flight performance and durability characteristic of ordinary two-piece solid golf balls, they are often in fact unfit for actual use.

Furthermore, these golf balls have generally been made to serve the needs of high head speed players, such as the professional golfer and the skilled amateur golfer. When they are used by low head speed players such as beginners, seniors and ladies, they are unsatisfactory both in terms of distance and feel.

Numerous studies have also been done on dimple characteristics, such as the dimple shape (e.g., depth and diameter), dimple configuration, and various dimple parameters, but there remains considerable room for improvement. The increasingly diverse and individualized desires of golfers have yet to be fully met.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a golf ball comprising a solid core, an intermediate layer, and a cover having a multiplicity of dimples, which golf ball is well balanced in hardness between the core, the intermediate layer and the cover, and given appropriate dimple characteristics, thus improving both the feel of the ball when hit with a club and the flight performance regardless of the club head speed.

We have found that, in a golf ball comprising a solid core, an intermediate layer, and a cover on the surface of which are formed a multiplicity of dimples, the flight distance and feel of the ball can be increased, regardless of the club head speed, by optimizing the ball construction, especially the balance in hardness between the core, the intermediate layer and the cover, and by also providing suitable dimple characteristics, particularly the total number of dimples, the dimple surface coverage, and the index Dst of the overall dimple surface area.

More specifically, we have discovered that, in a golf ball comprising a solid core, an intermediate layer, and a cover on the surface of which are formed a multiplicity of dimples, a ball construction having an optimal balance in hardness is obtained by providing the core with a Shore D hardness at the surface of up to 48, the intermediate layer with a Shore D hardness that is 53 to 60 and at least 8 Shore units higher than the surface hardness of the core, and the cover with a Shore D hardness that is 55 to 65 and higher than the hardness of the intermediate layer. Moreover, suitable dimple characteristics are obtained by forming, on the surface of a golf ball having the above-described construction, at least two types of dimples of different diameters and/or depths, by setting the total number of these dimples at 370 to 450, the ratio of the ball surface occupied by the dimples at 63% or more, and the index Dst of the overall dimple surface area at 4 or more, and also by setting the coefficient V_0 of the dimple cross-sectional shape at 0.37 to 0.55. These dimple characteristics, in combination with the optimized ball construction described above, provide a golf ball having a significantly improved flight distance and a good feel, regardless of the club head speed.

Accordingly, the present invention provides a golf ball comprising a solid core, an intermediate layer, and a cover on the surface of which are formed a plurality of dimples, wherein the core has a Shore D hardness at the surface of up to 48, the intermediate layer has a Shore D hardness of 53 to 60 which is at least 8 Shore units higher than the surface hardness of the core, the cover has a Shore D hardness of 55 to 65 which is higher than the hardness of the intermediate layer. The dimples are of at least two types having different diameters and/or depths, the total number of dimples is 370 to 450, the dimples cover at least 63% of the ball surface, and the index Dst of the overall dimple surface area is at least 4. Preferably, the coefficient V_0 of the dimple cross-sectional shape in this golf ball is 0.37 to 0.55, and the cover of the golf ball is made of a thermoplastic resin composed primarily of an ionomer resin.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view of a golf ball according to one embodiment of the invention.

FIG. 2 is schematic cross-sectional view of a dimple illustrating how to calculate V_0.

FIG. 3 is a perspective view of the same dimple.

FIG. 4 is a cross-sectional view of the same dimple.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, a golf ball 1 according to the present invention is shown as comprising a solid core 2 which is formed soft, an intermediate layer 3 which is harder than the surface of the core 2, and a cover 4 which is harder than the intermediate layer 3. A multiplicity of dimples (not shown) are formed on the surface of the cover 4.

The solid core has a surface hardness, as measured with a Shore D durometer, of up to 48, and preferably up to 45, but at least 30. A surface hardness greater than 48 gives too hard a core, which results in a ball having a short flight distance and a hard feel, particularly when driven by a low head speed golfer. The surface hardness of the solid core here refers to the average value for measurements taken at five points on the spherical surface of the solid core.

The diameter, specific gravity, and weight of the core are suitably adjusted insofar as the objects of the invention are attainable. Thus, the core preferably has a diameter of 30 to 39 mm, and especially 33 to 38 mm; a specific gravity of 1.10 and 1.30, and especially 1.13 to 1.25; and a weight of 25 to 35 g, and especially 26 to 33 g.

In the practice of the invention, no particular limit is imposed on the composition from which the solid core is formed. The solid core may be formed using a base rubber, a crosslinking agent, a co-crosslinking agent, an inert filler and other substances employed in the formation of conventional solid cores. The base rubber used herein may be any natural rubber and/or synthetic rubber conventionally used in solid golf balls, although 1,4-cis polybutadiene containing at least 40% cis structure is especially preferable in the invention. The polybutadiene may be blended with a suitable amount of natural rubber, polyisoprene rubber, styrene-butadiene rubber or the like if desired. Examples of crosslinking agents that can be used in the core-forming composition include organic peroxides such as dicumyl peroxide and di-t-butyl peroxide. The crosslinking agent is generally added in an amount of about 0.5 to 1.8 parts by weight per 100 parts by weight of the base rubber. Co-crosslinking agents that can be used include, without particular limitation, the metal salts of unsaturated fatty acids, and preferably the zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbons (e.g., acrylic acid and methacrylic acid), of which zinc acrylate is especially preferable. The amount of co-crosslinking agent added may be set as appropriate, although this amount is generally about 15 to 40 parts by weight per 100 parts by weight of the base rubber. Suitable inert fillers include zinc oxide, barium sulfate, silica, calcium carbonate and zinc carbonate, with zinc oxide and barium sulfate being most often used. The filler is usually included in an amount of up to 40 parts by weight per 100 parts by weight of the base

rubber, although this amount is governed in part by the specific gravities of the core and the cover, as well as weight standards for the ball, and is not subject to any particular limits. The overall hardness and weight of the core in the present invention may be set at optimum values by suitably adjusting the proportions in which the crosslinking agent and the filler (typically zinc oxide or barium sulfate) are added.

The core-forming composition obtained by combining the above components may be worked in a conventional mixer such as a Banbury mixer or a roll mill, then formed into a solid core of the above-indicated hardness using a core mold.

The intermediate layer 3 enclosing the core 2 has a Shore D hardness of 53 to 60, and preferably 54 to 59. A hardness of less than 53 fails to provide sufficient resilience, whereas a hardness of more than 60 results in a poor feel. The intermediate layer is formed to a Shore D hardness at least 8 units higher, and preferably 9 to 30 units higher, than the surface hardness of the core. A hardness difference of less than 8 units results in a golf ball having a poor feel and insufficient resilience.

The gage and specific gravity of the intermediate layer may be suitably adjusted insofar as the objects of the invention are attainable. Preferably, the gage (radial thickness) is 0.5 to 2.5 mm, and especially 1.0 to 2.3 mm; and the specific gravity is 0.90 to 1.18, and especially 0.91 to 1.16. The intermediate layer is not limited to one layer only, and may be formed as a plurality of layers.

Because the intermediate layer 3 serves to compensate for a loss of resilience in the core which is formed soft, it is preferably made of a material having, within the above-indicated range in hardness, an excellent resilience, typically an ionomer resin such as Himilan (manufactured by DuPont-Mitsui Polychemicals Co., Ltd.) or Surlyn (E. I. du Pont de Nemours & Co., Inc.). Thermoplastic resins other than ionomer resins which can be used in the intermediate layer include maleic anhydride-modified ethylene-alkyl unsaturated carboxylic acid ester copolymers such as HPR AR201 (DuPont-Mitsui Polychemicals Co., Ltd.), ethylene-unsaturated carboxylic acid-alkyl unsaturated carboxylic acid ester terpolymers such as Nucrel AN 4311 and AN 4307 (DuPont-Mitsui Polychemicals Co., Ltd.), polyester elastomers such as Hytrel 4047 (DuPont-Toray Co., Ltd.), polyamide elastomers such as Pebax 3533 (Atochem Inc.), and thermoplastic elastomers with crystalline polyethylene blocks such as Dynaron E6100P and E4600P (Japan Synthetic Rubber Co., Ltd.). These may be used alone or as mixtures of two or more thereof. Preferred compositions for the intermediate layer are obtained by blending 10 to 100% by weight, and especially 30 to 95% by weight, of the ionomer resin with 0 to 90% by weight, and especially 5 to 70% by weight, of a thermoplastic resin other than the ionomer resin.

In the resin composition for the intermediate layer, additives may be also incorporated which include inert fillers, typically zinc oxide or barium sulfate, as weight modifiers, and titanium dioxide for the purpose of coloration.

Any suitable method may be employed to cover the core 2 with this intermediate layer 3. For example, the interme-

diate layer may be formed about the core by surrounding the core with two hemispherical half-cups preformed from the intermediate layer composition and molding under applied heat and pressure, or by injection-molding the intermediate layer composition around the core.

The cover **4** enclosing the intermediate layer **3** is formed to a greater hardness than the intermediate layer. This must have a Shore D hardness of 55 to 65, and preferably 56 to 63. A cover having a hardness less than 55 fails to provide the golf ball with sufficient resilience, whereas a hardness higher than 65 results in a poor feel and poor control. The difference in Shore D hardness between the cover and the intermediate layer is preferably 1 to 10 units, and more preferably 2 to 8 units. A cover hardness lower than the hardness of the intermediate layer does not provide the ball with sufficient resilience and results in a poor feel.

The gage and specific gravity of the cover may be suitably adjusted insofar as the objects of the present invention are attainable. Preferably, the gage is 0.5 to 3.0 mm, and especially 1.0 to 2.3 mm, and the specific gravity is 0.90 to 1.18, and especially 0.91 to 1.15. Moreover, the cover is not limited to one layer only, and may be formed as two or more layers.

No limits are imposed on the cover composition. The cover may be formed of any well-known material having suitable properties as golf ball cover stock, although the use of a thermoplastic resin composed primarily of ionomer resin is preferable. Examples include Himilan 1557, 1605, 1855 and 1856 (DuPont-Mitsui Polychemicals Co., Ltd.). These may be used alone or as mixtures of two or more thereof.

UV absorbers, antioxidants, and dispersing aids such as metallic soaps may be added to the cover composition if necessary. Any suitable method may be employed to apply the cover over the intermediate layer, although this is generally done by surrounding the intermediate layer with two hemispherical cups preformed from the cover composition and molding under applied heat and pressure, or by injection-molding the cover composition around the intermediate layer.

As with conventional golf balls, the golf ball obtained in the above-described manner has a multiplicity of dimples formed on the surface. These dimples are of at least two types, and preferably of two to six types, having different diameters and/or depths. Preferably, the dimples have a diameter of 2.0 to 5.0 mm, and especially 2.2 to 4.5 mm, and a depth of 0.10 to 0.28 mm, and especially 0.11 to 0.25 mm. The total number of dimples is 370 to 450, and preferably 380 to 440. Dimples having a planar shape that is circular are preferred, although circularity is not critical and the dimples may also have elliptical, oval, petaloid, polygonal or other non-circular shapes.

In the golf ball of the invention, if one thinks of the ball as a sphere having an imaginary spherical surface, the ratio of the surface area of this imaginary sphere delimited by the edges of the individual dimples to the entire surface area of the imaginary sphere, sometimes referred to herein as the dimple surface coverage, is at least 63% of the surface of the ball, and preferably 65 to 79%. A dimple surface coverage of less than 63% fails to provide the golf ball with a sufficient flight distance.

The dimples in the invention are formed such that the dimple cross-sectional shape coefficient V_0, which is understood here to be the average value obtained for all the dimples when the volume of space in a dimple below a planar surface circumscribed by the edge of the dimple is divided by the volume of a cylinder whose base is the planar surface and whose height is the maximum depth of that particular dimple from this base, is 0.37 to 0.55, and preferably 0.39 to 0.53.

The value V_0 indicates the proportion of the volume that individual dimples essentially occupy on the golf ball. This value is described in greater detail. Reference is made first to cases in which the planar shape of the dimple is circular. In the cross-section of FIG. **2**, viewed radially with respect to the ball center, an imaginary sphere **6** having the diameter of the ball and an imaginary sphere **7** having a diameter 0.16 mm smaller than the ball diameter are drawn in conjunction with a dimple **5**. The circumference of sphere **7** intersects the dimple **5** at two points **8**. The tangents **9** to the dimple **5** at these points **8**, extended outward, intersect imaginary sphere **6** at points **10**. A series of such intersections **10** defines the dimple edge. The dimple edge is so defined for the reason that the exact position of the dimple edge cannot be otherwise determined because the actual edge of a dimple **5** is generally rounded. As shown in FIGS. **3** and **4**, the dimple edge **11** circumscribes a planar surface **12** (a circle having a diameter D_m). The dimple space **13** below this planar surface **12** has a volume V_P which is calculated using the equation shown below. A cylinder **14** whose base is the planar surface **12** and whose height is the maximum depth D_P of the dimple from this planar surface **12** or base has a volume V_Q which is calculated using the equation shown below. The V_0 value is obtained by calculating the ratio of the dimple space volume V_P to the cylinder volume V_Q, and determining the average of this ratio for all the dimples on the ball surface.

$$V_P = \int_0^{\frac{Dm}{2}} 2\pi xy\,dx$$

$$V_Q = \frac{\pi Dm^2 Dp}{4}$$

$$V_0 = \frac{V_P}{V_Q}$$

In cases where the planar shape of the dimple is not circular, the maximum diameter of the dimple (or the maximum length of the planar surface) is determined, and the planar surface of the dimple is assumed to be a circle having a diameter equal to this maximum diameter (or maximum length), whereupon V_0 can be calculated as above. Where a plurality of dimple types having different diameters and/or depths are formed on the golf ball, V_0 is determined for each type of dimple, and these values are averaged to give the coefficient V_0 of the dimple cross-sectional shape for the entire ball.

Also, letting n be the number of types of dimples formed on the ball surface, and D_{mk}, D_{pk} and Nk (where k=1,2,3, . . . n) be respectively the diameter, maximum depth and number of each type of dimple, the golf balls of the invention are preferably formed such that the index Dst of the overall dimple surface area, as given by the equation

shown below, is at least 4.0, and preferably 4.2 to 10.0. This index Dst optimizes the various dimple parameters. When the index Dst is less than 4.0, the synergistic effect due to optimal ball construction and optimized dimple parameters that is the aim of this invention fails to be achieved, resulting in a poor flight performance.

$$Dst = \frac{n\sum_{k=1}^{n}[(D_{mk}^2 + D_{pk}^2) \times V_0k \times Nk]}{4R^2}$$

Note that R in the formula is the radius of the golf ball, V_0 is as defined above, and Nk is the number of dimples k.

Thus, by optimizing the ball construction, and especially the balance in hardness between the core, the intermediate layer and the cover, and by also optimizing the parameters of the dimples formed on the surface of a ball with this type of construction, and in particular the overall number of dimples, the dimple surface coverage and the index Dst of overall dimple surface area, the present invention provides a golf ball having a significantly improved flight distance and an excellent feel upon impact, regardless of the head speed of the club with which the ball is hit.

EXAMPLES

Examples of the invention are given below by way of illustration, and are not intended to limit the scope of the invention.

Examples 1–4 and Comparative Examples 1–5

Solid cores (a) to (f) were prepared by kneading the core compositions shown in Table 1, then vulcanizing the kneaded compositions within a mold at 155° C. for about 20 minutes. The surface hardness of a core is the average of five values measured at random points on the core surface with a Shore D durometer.

Next, using materials A to H in Table 2 for the intermediate layer and the cover, first the intermediate layer was injection-molded onto the surface of the core, then the cover was injection-molded around this intermediate layer. This was done in accordance with the core, intermediate layer and cover combinations shown in Table 4. Dimples as specified in Table 3 were formed on the surface of the cover at this time. The properties and performance of the golf balls thus obtained in Examples 1 to 4 and Comparatives Examples 1 to 5 are shown in Table 4. The results for distance and feel shown in Table 4 were determined by the methods described below. The finished balls all had a weight of 45.20±0.20 g and a diameter of 42.70±0.05 mm.

Distance

Using a swing robot manufactured by True Temper Co., the golf balls were measured for carry and total distance when hit with a driver (#W1) at head speeds of 45 m/s (HS 45) and 35 m/s (HS 35). The driver used at HS45 was a PRO 230 Titan having a loft angle of 10°, while that used at HS35 was a PRO 230 Titan LD having a loft angle of 13° (both manufactured by Bridgestone Sports Co., Ltd.).

Feel

The balls were driven by three golfers with a head speed of 45 m/s (45 HS) and three golfers with a head speed of 35 m/s (35 HS), who then rated each ball according to the following criteria.

S: soft

RS: rather soft

RH: rather hard

H: hard

TABLE 1

Core formulation (parts by weight)	a	b	c	d	e	f
cis-1,4-Polybutadiene	100	100	100	100	100	100
Zinc acrylate	25	21.5	19.5	18.5	34	41
Dicumyl peroxide	0.6	0.6	0.6	0.6	0.6	0.6
Peptizer	1	1	1	1	1	1
Antioxidant	0.1	0.1	0.1	0.1	0.1	0.1
Zinc oxide	29.7	31	31.8	34.5	26.3	23.7

TABLE 2

Intermediate layer and cover material (parts by weight)	A	B	C	D	E	F	G	H
Himilan 1557*1						50		
Himilan 1605*1	35		42			50		50
Himilan 1650*1							75	
Himilan 1706*1	35		42				25	50
Himilan 1855*1					50			
Himilan 1856*1					50			
Himilan AM7311*1				37				
Surlyn 7930*2				37				
Surlyn 8511*2		35						
Surlyn 8512*2		35						
Dynaron E6100P*3		30	16					
Dynaron E4600P*3	30							
Nucrel AN4311*4				26				

*1 An ionomer resin manufactured by DuPont Mitsui Polychemicals Co., Ltd.
*2 An ionomer resin manufactured by E.I. du Pont de Nemours & Co., Inc.
*3 A hydrogenated polybutadiene block copolymer of E-EB-E system manufactured by Japan Synthetic Rubber Co., Ltd.
*4 An ethylene-methacrylic acid-acrylate terpolymer manufactured by Dupont-Mitsui Polychemicals Co., Ltd.

TABLE 3

Type of dimple	Diameter (mm)	Depth (mm)	V_0	Number	Total number	Surface coverage (%)	Dst
I	4.00	0.175	0.51	276	396	76.5	6.3
	3.60	0.150	0.51	24			
	3.25	0.140	0.51	60			
	2.45	0.125	0.51	36			
II	3.80	0.175	0.52	264	432	72.8	4.5
	3.20	0.150	0.49	120			
	2.35	0.125	0.48	48			
III	4.10	0.185	0.48	72	392	78.5	4.5
	3.90	0.175	0.48	200			
	3.50	0.155	0.48	120			
IV	3.40	0.195	0.49	360	500	68.6	2.7
	2.45	0.195	0.49	140			
V	3.95	0.240	0.40	240	360	67.2	2.2
	3.10	0.240	0.40	120			

TABLE 4

		Examples				Comparative Examples				
		1	2	3	4	1	2	3	4	5
Core	Type	a	b	c	d	d	e	a	d	f
	Diameter (mm)	36.5	36.5	36.5	35.7	35.7	36.5	36.5	36.5	36.5
	Specific gravity	1.22	1.22	1.22	1.23	1.23	1.22	1.22	1.23	1.22
	Surface hardness H1 (Shore D)	48	42	38	35	35	55	48	35	60
Intermediate layer	Type	C	B	B	C	C	D	C	H	B
	Surface hardness H2 (Shore D)	58	55	55	58	58	60	58	65	55
	Gage (mm)	1.6	1.6	1.6	2.0	2.0	1.6	1.6	1.6	1.6
Hardness difference (H2 – H1)		10	13	17	23	23	5	10	30	–5
Cover	Type	F	E	F	F	F	G	H	A	F
	Surface hardness H3 (Shore D)	60	58	60	60	60	61	65	53	60
	Gage (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Hardness difference (H3 – H2)		2	3	5	2	2	1	7	–12	5
Type of dimple		I	II	III	II	IV	II	V	IV	V
HS45 #W1	Carry (m)	213.0	211.0	212.0	210.0	208.0	211.5	207.0	206.5	207.5
	Total distance (m)	230.0	228.5	228.0	227.0	222.0	227.5	220.0	221.0	222.5
HS35 #W1	Carry (m)	148.0	149.0	149.5	150.0	147.0	145.0	146.0	147.0	144.0
	Total distance (m)	155.0	156.0	156.0	156.5	152.0	148.5	149.0	151.0	148.0
Feel	HS45	S	S	S	S	S	RS	S	RH	H
	HS35	S	S	S	S	S	RH	S	RH	H

As is apparent from the results in Table 4, the golf ball of Comparative Example 1, which shares the same characteristics as the golf ball of Example 4 within the invention, except for the dimple parameters, has a good feel upon impact, but the Dst index is low on account of a greater number of dimples, resulting in too short a distance. The golf ball of Comparative Example 2 has a core with a high surface hardness and a less hardness difference between the core and the intermediate layer, as a result of which the distance and feel of the ball when hit at a low head speed are poor. The golf ball of Comparative Example 3, aside from its very low Dst index, satisfies the conditions of the invention, which accounts for its good feel but its short distance. The golf ball of Comparative Example 4 has an intermediate layer that is very hard, harder in fact than the cover, as well as a greater overall number of dimples, on account of which the Dst value is too low, resulting in both a poor distance and a poor feel. The golf ball of Comparative Example 5 has a core that is very hard, and indeed harder than the intermediate layer, as well as a low Dst index, resulting in too short a distance and a hard feel.

By contrast, the golf balls of Examples 1 to 4 within the scope of the invention demonstrated a satisfactory distance and a good feel regardless of the club head speed.

Japanese Patent Application No. 136101/1997 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

We claim:

1. A golf ball comprising a solid core, an intermediate layer, and a cover on the surface of which are formed a plurality of dimples, wherein

the core has a Shore D hardness at the surface of up to 48, the intermediate layer has a Shore D hardness which is 53 to 60 and at least 8 Shore units higher than the surface hardness of the core, and the cover has a Shore D hardness which is 55 to 65 and higher than the hardness of the intermediate layer,

the dimples are of at least two types having different diameters and/or depths,

the total number of dimples is 370 to 450,

the dimples cover at least 63% of the ball surface, and

the index Dst of the overall dimple surface area is at least 4.

2. The golf ball of claim 1 wherein the coefficient V_0 of the dimple cross-sectional shape is 0.37 to 0.55.

3. The golf ball of claim 1 wherein the cover is made of a thermoplastic resin composed primarily of an ionomer resin.

* * * * *

Exhibit D

US005872185A

United States Patent [19]

Ichikawa et al.

[11] Patent Number: 5,872,185

[45] Date of Patent: Feb. 16, 1999

[54] **GOLF BALL**

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[21] Appl. No.: **921,615**

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[51] **Int. Cl.**[6] **C08L 33/02**; C08L 53/00; C08L 53/02; A63B 37/12

[52] **U.S. Cl.** **525/93**; 473/373; 473/374

[58] **Field of Search** 525/93; 473/373, 473/374

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,919,434 4/1990 Saito .
5,559,188 9/1996 Egashira 525/221

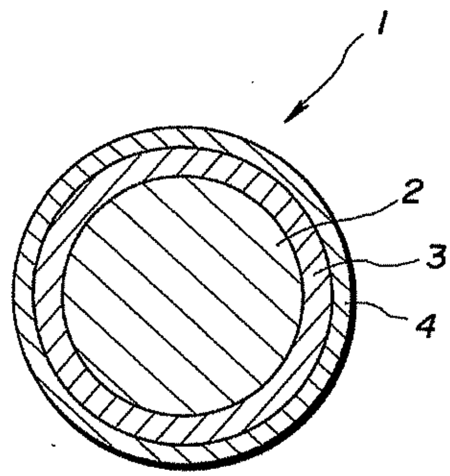
Primary Examiner—David Buttner
Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC

[57] **ABSTRACT**

In a golf ball comprising a core, an intermediate layer, and a cover, the intermediate layer is formed of a resin component consisting essentially of 10–60 parts by weight of a thermoplastic elastomer having a crystalline polyethylene block and 90–40 parts by weight of an ionomer resin having a melt index of 3–20 g/10 min. at 190° C. The resin component is easily moldable into a highly resilient intermediate layer. The ball has improved flight performance, durability and feel.

17 Claims, 1 Drawing Sheet

FIG.1



GOLF BALL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a golf ball comprising a core, an intermediate layer, and a cover. More particularly, it relates to such a golf ball in which a resilient intermediate layer is formed of an easily moldable resin component consisting essentially of a mixture of a thermoplastic elastomer and an ionomer resin so that the ball may have excellent flight performance and pleasant hitting feel as well as improved durability against hitting.

2. Prior Art

Golf balls of various structures are on the market. Among others, two-piece solid golf balls having a rubber base core enclosed with a cover of ionomer resin or the like and thread-wound golf balls comprising a wound core having thread rubber wound around a solid or liquid center and a cover enclosing the core share the majority of the market.

Most amateur golfers are fond of two-piece solid golf balls which have excellent flying performance and durability although these balls have the disadvantages of a hard feel on hitting and low control due to quick separation from the club head on hitting. For this reason, many professional golfers and low handicap amateur golfers prefer wound golf balls to two-piece solid golf balls. The wound golf balls are superior in feeling and control, but inferior in flight distance and durability to the two-piece solid golf balls.

Under the present situation that two-piece solid golf balls and wound golf balls have contradictory characteristics as mentioned above, players make a choice of golf balls depending on their own skill and preference.

Various attempts have been made to solve the above-mentioned problems. One attempt is to interpose a resin layer or intermediate layer between the core and the cover to impart various properties. For example, U.S. Pat. No. 4,431,193 discloses a golf ball comprising a core, an intermediate layer formed of a hard, high flexural modulus ionomer resin, and a cover formed of a soft, low flexural modulus ionomer resin. The intermediate layer of hard resilient ionomer resin compensates for a loss of resilience inherent to the use of a soft cover. The golf ball of this patent, however, has the problems of a hard hitting feel and substantially deteriorated durability against repetitive hitting because a very hard, high or moderate acid content ionomer resin is used as the intermediate layer.

As one solution, U.S. Pat. No. 4,884,814 proposes to reduce the hardness of an ionomer resin in the intermediate layer. The golf ball of this patent, however, is low in restitution and fails to provide satisfactory flight performance.

None of the golf balls having an intermediate layer between the core and the cover have reached a fully satisfactory level. There is a need for further improvement and development.

Therefore, an object of the present invention is to provide a golf ball comprising a core, an intermediate layer and a cover in which an easily moldable, highly resilient material is used as the intermediate layer so as to improve the adhesion of the intermediate layer to both the core and the cover and improve the flight performance, hitting durability, and hitting feel of the ball.

SUMMARY OF THE INVENTION

Regarding a golf ball comprising a core, an intermediate layer and a cover, the inventors have found that when the

resin component of which the intermediate layer is formed is mainly a mixture of a thermoplastic elastomer having a crystalline polyethylene block and an ionomer resin, the intermediate layer is improved in moldability and resilience and the golf ball has excellent flight performance, excellent durability, and a very soft hitting feel.

More particularly, regarding a golf ball comprising a core, an intermediate layer enclosing the core, and a cover enclosing the intermediate layer, the inventors have found that when a resin component based on a mixture of 10 to 60 parts by weight of a thermoplastic elastomer having a crystalline polyethylene block and 90 to 40 parts by weight of an ionomer resin is used, there is obtained an intermediate layer having a high degree of resilience which is not achievable with conventional blends of ionomer resins. The ball as a whole is outstandingly improved in resilience. Additionally, upon full shots with a driver, the ball receives an optimum spin rate to travel a drastically increased distance and gives a very soft pleasant hitting feel.

The inventors have further found that when an ionomer resin having a melt index of at least 3 g/10 min. at 190° C. is used as the ionomer resin to be blended with the thermoplastic elastomer in the intermediate layer, even a blend thereof with a larger proportion of a thermoplastic elastomer having a low melt index is easily moldable to form the intermediate layer without molding defects such as weld lines, sink marks and short shots. In addition, the intermediate layer is improved in adhesion to both the core and the cover and serves as a buffer for the hardness difference between the core and the cover, improving the durability of the ball against repetitive hits. The invention is predicated on this finding.

It is noted that U.S. Pat. No. 5,559,188 assigned to the same assignee as the present invention or JP-A 767/1996 discloses a golf ball comprising a core and a cover wherein the cover is formed of a resin component consisting essentially of 10 to 60 parts by weight of a thermoplastic elastomer having a crystalline polyethylene block and 90 to 40 parts by weight of an ionomer resin. The present invention uses a mixture of a thermoplastic elastomer having a crystalline polyethylene block and an ionomer resin as the intermediate layer rather than the cover and forms a cover, typically of an ionomer resin thereon, thereby providing a golf ball which is further increased in flight distance and drastically improved in durability.

According to the invention, there is provided a golf ball comprising a core, an intermediate layer enclosing the core, and a cover enclosing the intermediate layer wherein the intermediate layer comprises a resin component based on a mixture of 10 to 60 parts by weight of a thermoplastic elastomer having a crystalline polyethylene block and 90 to 40 parts by weight of an ionomer resin having a melt index of at least 3 g/10 min. at 190° C.

Preferably, the thermoplastic elastomer is a thermoplastic elastomer having a polyethylene block or a polyethylene block and a polystyrene block as a hard segment and an ethylene/butylene random copolymer as a soft segment. More preferably, the thermoplastic elastomer comprises a hydrogenated product of polybutadiene or styrene/butadiene copolymer. Preferably, the thermoplastic elastomer has a melt index of 0.01 to 15 g/10 min. at 230° C. and a surface hardness of 10 to 50 in Shore D. Further preferably, the intermediate layer has a Shore D hardness of 48 to 62.

Preferably, the ionomer resin is a mixture of an ionomer resin having a monovalent metal and an ionomer resin having a divalent metal and has a Shore D hardness of 60 to 70.

Preferably, the golf ball experiences a distortion of 2.5 to 4 mm under a constant load of 100 kg.

Preferably, the cover is mainly formed of an ionomer resin and has a Shore D hardness of 50 to 68.

BRIEF DESCRIPTION OF THE DRAWINGS

The only figure, FIG. 1 is a schematic cross-sectional view of a golf ball according to one embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, the golf ball of the invention generally designated at 1 is illustrated as comprising a spherical core 2, an intermediate layer 3 formed on the surface of the core 2, and a cover 4 surrounding the surface of the core 2, and intermediate layer 3. According to the invention, the intermediate layer 3 is formed of a resin component primarily comprising a mixture of a thermoplastic elastomer having a crystalline polyethylene block and a high melt index ionomer resin.

In the resin component of which the intermediate layer is formed, the thermoplastic elastomer having a crystalline polyethylene block used herein is a thermoplastic elastomer having a crystalline polyethylene block (E) or a crystalline polyethylene block (E) and a crystalline polystyrene block (S) as a hard segment and a relatively random copolymer (EB) structure consisting of ethylene and butylene as a soft segment. The preferred thermoplastic elastomers are block copolymers of a molecular structure having the hard segment at one end or both ends thereof, typically E-EB, E-EB-E, and E-EB-S structures.

These thermoplastic elastomers are obtained by hydrogenating polybutadiene and styrene-butadiene copolymers. The polybutadiene and styrene-butadiene copolymers to be hydrogenated are preferably butadiene polymers having 1,4-polymerized blocks with a 1,4-bond content of 95 to 100% by weight and containing 50 to 100% by weight, especially 80 to 100% by weight of 1,4-bond based on the entire weight of butadiene structure. In particular, thermoplastic elastomers of the E-EB-E type are obtained by hydrogenating polybutadiene wherein both ends of its molecular chain are 1,4-polymers rich in 1,4-bond and an intermediate portion is a mixture of 1,4-bond and 1,2-bond. The percent hydrogenation of hydrogenated products of polybutadiene and styrene-butadiene copolymers (that is, percent conversion of double bonds in polybutadiene and styrene-butadiene copolymers into saturated bonds) is preferably 60 to 100%, more preferably 90 to 100%. With a percent hydrogenation of less than 60%, gelation and deterioration would occur in blending a hydrogenated polybutadiene with an ionomer resin and problems would arise with respect to the hitting durability of the resulting intermediate layer.

Preferably the thermoplastic elastomers contain about 10 to 50% by weight of the hard segment. Elastomers containing more than 50% by weight of the hard segment would be less flexible, failing to achieve the objects of the invention. With less than 10% by weight of the hard segment, a blend would be less moldable.

The thermoplastic elastomer should preferably have a melt index of 0.01 to 15 g/10 min. at 230° C., more preferably 0.03 to 10 g/10 min. at 230° C. from the standpoint of preventing defects such as weld lines, sink marks and short shots upon injection molding.

Further preferably, the thermoplastic elastomer has a surface hardness of 10 to 50 in Shore D. A thermoplastic elastomer having a surface Shore D hardness of less than 10, which indicates a less content of terminal crystalline polyethylene, would be less compatible with an ionomer resin so that the resulting ball might lose durability against repetitive hits. A thermoplastic elastomer having a surface Shore D hardness of more than 50 would be less resilient and a blend thereof with an ionomer resin would also be less resilient.

The thermoplastic elastomers preferably have a number average molecular weight of about 30,000 to 800,000.

The thermoplastic elastomers having a crystalline polyethylene block are commercially available, for example, under the trade name of DYNARON E6100P, HSB604, and E4600P from Nihon Synthetic Rubber K.K. They may be used alone or in admixture of two or more. Especially DYNARON E6100P which is a block polymer having a crystalline ethylene block at each end is useful in the practice of the invention.

The ionomer resin to be blended with the thermoplastic elastomer should have a melt index of at least 3 g/10 min. at 190° C., preferably 3 to 20 g/10 min. at 190° C., more preferably 4 to 15 g/10 min. at 190° C. If the melt index of the ionomer resin is less than 3 g/10 min. at 190° C., a corresponding resin blend would be too low in melt flow so that the mold cavity might not be fully filled with the resin blend, resulting in the intermediate layer with molding defects such as weld lines, sink marks and short shots.

When an ionomer resin having such a high melt index is used, even a blend thereof with a larger proportion of a thermoplastic elastomer having a low melt index, especially DYNARON E6100P (melt index 0.6 g/10 min. at 230° C.) is easily moldable to form the intermediate layer without molding defects such as weld lines, sink marks and short shots. In addition, the intermediate layer is improved in adhesion to both the core and the cover, eventually improving the durability of the ball against repetitive hits.

It is noted that the melt index (M.I.) is indicative of the melt flow of a thermoplastic resin as measured according to JIS K 7210. The melt index of an ionomer resin is expressed by the amount (in gram) of the resin extruded for 10 minutes at 190° C. under a load of 2,160 grams. The melt index of an thermoplastic elastomer is expressed by the amount (in gram) of the elastomer extruded for 10 minutes at 230° C. under a load of 2,160 grams.

The ionomer resins are preferably copolymers of α-olefin and α,β-unsaturated carboxylic acid wherein the carboxyl group is neutralized with a metal ion (e.g., Na, Li, Zn, Mg, and K ions). Examples of the α-olefin include those having a few carbon atoms such as ethylene and propylene. Examples of the α,β-unsaturated carboxylic acid include acrylic acid, methacrylic acid, maleic acid and fumaric acid, with acrylic acid and methacrylic acid being preferred. The binary copolymers of α-olefin and α, β-unsaturated carboxylic acid desirably contain 5 to 20% by weight of the α,β-unsaturated carboxylic acid. Preferably the degree of neutralization with metal ions is 10 to 90 mol % of the acid group.

Preferably a mixture of a first ionomer resin having a monovalent metal and a second ionomer resin having a divalent metal is used as the ionomer resin from the standpoint of improving resilience. In the mixture, the weight ratio of the first to the second ionomer resin is preferably between 20/80 and 80/20. Typically the monovalent metal is sodium (Na) and the divalent metal is zinc (Zn).

The ionomer resin used herein is not critical insofar as its melt index (at 190° C.) is within the above-defined range. Commercially available ionomer resins, for example, Surlyn AD8511 and AD8512 from E. I. duPont de Nemours & Co. may be used alone or in admixture of two or more. Where a blend of two or more ionomer resins is used, the blend should have a melt index (at 190° C.) within the above-defined range. From the standpoint of improving resilience, the ionomer resin or ionomer resin blend should preferably have a Shore D hardness of 60 to 70, especially 62 to 67.

In the practice of the invention, the thermoplastic elastomer having a crystalline polyethylene block and the ionomer resin should be blended such that the blend contains 10 to 60 parts by weight, preferably 16 to 50 parts by weight of the thermoplastic elastomer and 90 to 40 parts by weight, preferably 84 to 50 parts by weight of the ionomer resin provided that the total of the two components is 100 parts by weight. Blending less than 10 parts by weight of the thermoplastic elastomer is insufficient for softening purposes so that hitting feel and durability are not fully improved. More than 60 parts by weight of the thermoplastic elastomer detracts from resilience.

Although the intermediate layer is mainly composed of a mixture of the thermoplastic elastomer and the ionomer resin according to the invention, various additives such as pigments, dispersants, and antioxidants may be added to the resin component if necessary.

The intermediate layer preferably has a Shore D hardness of 48 to 62, more preferably 50 to 58. An intermediate layer with a Shore D hardness of less than 48 would be less resilient whereas an intermediate layer with a Shore D hardness of more than 62 would fail to improve hitting feel and controllability and maintain durability.

The thickness and specific gravity of the intermediate layer may be properly adjusted insofar as the object of the invention is attainable. Preferably the thickness is 1 to 3 mm, especially 1.2 to 2.5 mm, and the specific gravity is 0.9 to 1.3, especially 0.95 to 1.2.

The core **2** to be enclosed with the intermediate layer **3** is not critical and may be either a solid core or a wound core although the solid core is preferred. The wound core may have either a solid center or a liquid center. The wound core or solid core may be produced from a well-known material by a conventional technique.

No particular limits are imposed on the hardness, diameter, weight and specific gravity of the core insofar as the object of the invention is attainable. For example, the solid core may have a hardness corresponding to a distortion of 2.8 to 4.5 mm, especially 3 to 4.5 mm under a constant load of 100 kg, a diameter of 34.3 to 38.7 mm, especially 34.7 to 37.9 mm, and a weight of 28.5 to 35 grams, especially 29.5 to 33 grams.

Any desired method may be employed in enclosing the core with the intermediate layer. For example, the resin component is directly injection molded around the core. Alternatively, a pair of hemispherical half cups are formed from the resin component, and the core is encased in the half cups, which are heat compression molded at 110 to 160° C. for 2 to 10 minutes. Particularly when the intermediate layer is formed around the core by injection molding, the molding of the intermediate layer is effectively accomplished without leaving molding defects such as weld lines, sink marks and short shots for the reason that the resin component of the intermediate layer contains a high melt index ionomer resin.

The cover **4** is preferably composed mainly of an ionomer resin, for example, Surlyn 8120 (E. I. duPont) and Himilan 1605, 1855, 1557, 1601 and 1706 (Mitsui duPont Polychemical K.K.). Another thermoplastic resin may be blended with the ionomer resin in such an amount that the physical

properties of a golf ball may not be impaired, for example, less than 10% by weight, especially less than 5% by weight of the entire cover stock. Further, if necessary, various additives such as pigments, dispersants, antioxidants and UV absorbers may be added to the cover stock in conventional amounts.

The cover stock should preferably have a surface hardness of 50 to 68, more preferably 50 to 63, most preferably 54 to 60 on Shore D hardness scale. A cover with a Shore D hardness of less than 50 would be less resilient and adversely affect the flight distance whereas a cover with a Shore D hardness of more than 68 would fail to improve hitting feel and controllability and maintain durability. The cover preferably has a (radial) thickness of 1 to 3 mm, more preferably 1.2 to 2.5 mm. The total thickness of the intermediate layer and the cover is preferably at least 2 mm, more preferably 2 to 4.2 mm. A total thickness of less than 2 mm would lead to a loss of durability against hitting.

By forming a cover from a cover stock containing at least 90% by weight, preferably at least 95% by weight, especially at least 97% by weight of the ionomer resin to a Shore D hardness of 50 to 68 and combining this cover with the above-mentioned intermediate layer, there is obtained a golf ball which will travel an increased distance and is outstandingly durable against hitting.

Any desired method may be used in forming the cover on the intermediate layer. For example, the cover stock is directly injection molded around the intermediate layer. Alternatively, the cover stock is molded into a pair of hemispherical half-cups, and the core with the intermediate layer is encased in the half-cups, which are heat compression molded at 110 to 160° C. for 2 to 10 minutes.

The golf ball may be indented in its cover surface with dimples in a conventional manner. At the end of molding, the ball is subject to surface finishing treatments such as buffing, painting and stamping.

The golf ball according to the invention is of the above-mentioned construction. The golf ball preferably has a hardness corresponding to a distortion of 2.5 to 4 mm, especially 2.8 to 3.5 mm under a constant load of 100 kg. Other ball parameters including weight and diameter may be properly determined in accordance with the Rules of Golf.

There has been described a golf ball having an intermediate layer composed mainly of a blend of a thermoplastic elastomer having a crystalline polyethylene block and a high melt index ionomer resin in a specific ratio. The intermediate layer is easily moldable and has high resilience or restitution. The ball had the advantages of improved flight performance, improved durability against hitting, and pleasant hitting feel.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation. All the amounts of components used in the solid core, intermediate layer, and cover are expressed in parts by weight.

Examples 1–9 and Comparative Examples 1–7

For the manufacture of three-piece solid golf balls, solid cores A, B, and C as shown in Table 1 were prepared by milling a rubber composition of the formulation shown in Table 1 and molding and vulcanizing it in a mold at 160° C. for 20 minutes. The cores were measured for hardness as a distortion (mm) under a constant load of 100 kg. The results are shown in Tables 2 and 3.

TABLE 1

	A	B	C
Cis-1,4-polybutadiene*1	100	100	100
Zinc diacrylate	27	26	28
Zinc oxide	28	22	21.5
Antioxidant	0.1	0.1	0.1
Dicumyl peroxide	1	1	1
Zn salt of pentachlorothiophenol	1	1	1

*1JSR BR01 by Nihon Synthetic Rubber K.K.

Next, an intermediate layer-forming composition and a cover composition were prepared by milling components of the formulation shown in Tables 2 and 3 and injection molded around the solid core and the intermediate layer, respectively, obtaining golf balls of Examples 1 to 9 and Comparative Examples 1 to 7 are reported in Tables 2 and 3. It is noted that Comparative Examples 1 and 2 were two-piece solid golf balls free of the intermediate layer.

The golf balls were examined for moldability of the intermediate layer, initial velocity, ball hardness, flight performance, hitting feel, and durability against hitting by the following tests. The results are shown in Tables 2 and 3.

Moldability of the intermediate layer

After the intermediate layer-forming composition was injected molded on the surface of the core, the intermediate layer was observed for molding defects.

O: neither weld lines nor sink marks occurred

X: weld lines and sink marks occurred

Initial velocity

An initial velocity (m/s) was measured according to the measurement method of USGA (or R&A).

Ball hardness

Hardness is expressed by a distortion (mm) of a ball under a constant load of 100 kg.

Flight performance

Using a hitting machine by True Temper Co. equipped with a driver (#W1), a ball was actually struck at a head speed of 45 m/sec. (HS45) to measure a spin rate, carry and total distance. The club used was PRO 230TITAN driver by Bridgestone Sports Co., Ltd. with loft angle 11°, shaft Harmotech-lite, HM50J (HK), hardness S, and balance D2.

Hitting feel

An actual hitting test was performed on a ball by a panel of five professional golfers with a head speed of 45 m/sec. (HS45). The ball was rated by the following criterion.

O: soft

X: hard

Durability against hitting

A ball was successively hit 300 times at a head speed of 38 m/sec. before it was observed for surface cracks.

TABLE 2

	Example								
	1	2	3	4	5	6	7	8	9
Core									
Core type	A	A	A	A	A	A	A	A	A
Hardness (mm)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
Intermediate layer									
AD8511*2	25	35	42	35	25	35	42	42	35
AD8512*2	25	35	42	35	25	35	42	42	35
D6100P*3	50	30	16	30	—	—	—	16	30
D4600P*3	—	—	—	—	50	30	16	-	—
Resin hardness (Shore D)	50	56	58	56	50	53	56	58	56
Gage (mm)	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Moldability	O	O	O	O	O	O	O	O	O
Cover									
H1605*4	—	—	—	25	—	—	—	—	50
S8120*2	—	—	—	—	—	—	—	50	—
H1855*4	—	—	—	—	—	—	—	30	—
H1557*4	50	50	50	50	50	50	50	20	—
H1601*4	50	50	50	25	50	50	50	—	—
H1706*4	—	—	—	—	—	—	—	—	50
Resin hardness (Shore D)	59	59	59	60	59	59	59	54	63
Gage (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Ball									
Outer diameter (mm)	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7
Weight (g)	45.3	45.3	45.3	45.3	45.3	45.3	45.3	45.3	45.3
Hardness (mm)	3.3	3.0	2.8	2.9	3.3	3.2	3.0	3.0	2.8
Initial velocity (m/s)	76.9	77.1	77.2	77.3	77.0	77.1	77.2	76.8	77.4
Test									
#W1/HS45									
Spin (rpm)	2510	2560	2610	2510	2500	2550	2610	2800	2400
Carry (m)	217.5	218.0	218.5	218.0	218.0	218.5	218.5	218.0	218.5
Total (m)	226.5	226.5	227.0	227.0	227.0	227.0	227.0	226.0	227.5
Hitting feel	O	O	O	O	O	O	O	O	O
Durability against 300 hits	no cracks	no cracks	no cracks	no cracks	no cracks	no cracks	no cracks	no cracks	no cracks

TABLE 3

	Comparative Example						
	1	2	3	4	5	6	7
Core							
Core type	B	C	A	A	A	A	A
Hardness (mm)	4.0	3.8	3.8	3.8	3.8	3.8	3.8
Intermediate layer							
AD8511*2	—	—	25	35	42	50	—
AD8512*2	—	—	25	35	42	50	—
D6100P*3	—	—	—	—	—	—	50
S8320*2	—	—	25	15	8	—	—
S9320*2	—	—	25	15	8	—	—
H1706*4	—	—	—	—	—	—	25
H1605*4	—	—	—	—	—	—	25
Resin hardness (Shore D)	—	—	50	56	58	63	50
Gage (mm)	—	—	1.6	1.6	1.6	1.6	1.6
Moldability	—	—	○	○	○	○	X
Cover							
H1706*4	—	35	—	—	—	—	—
H1605*4	—	35	—	—	—	—	—
D6100P*3	—	30	—	—	—	—	—
S8120*2	—	—	—	—	—	50	—
H1855*4	—	—	—	—	—	30	—
H1557*4	50	—	50	50	50	20	50
H1601*4	50	—	50	50	50	—	50
Resin hardness (Shore D)	59	56	59	59	59	54	59
Gage (mm)	2.0	2.0	1.5	1.5	1.5	1.5	1.5
Ball							
Outer diameter (mm)	42.7	42.7	42.7	42.7	42.7	42.7	42.7
Weight (g)	45.3	45.3	45.3	45.3	45.3	45.3	45.3
Hardness (mm)	3.1	3.0	3.3	3.0	2.8	2.5	3.3
Initial velocity (m/s)	76.9	76.9	76.3	76.6	76.8	77.2	76.9
Test							
#W1/HS45							
Spin (rpm)	2510	2700	2510	2560	2610	2700	2520
Carry (m)	217.0	217.0	216.0	216.5	217.0	218.5	217.0
Total (m)	225.0	225.0	223.0	223.5	224.0	227.0	227.0
Hitting feel	○	○	○	○	○	X	○
Durability against 300 hits	cracked	cracked	no cracks	no cracks	no cracks	cracked	no cracks

*2 ionomer resins by E. I. duPont de Nemours & Co.
AD8511: Zn salt, Shore D hardness 61, M.I. 5.3 g/10 min. (190° C.)
AD8512: Na salt, Shore D hardness 63, M.I. 4.8 g/10 min. (190° C.)
S8120: Na salt, Shore D hardness 45, M.I. 1.0 g/10 min. (190° C.)
S8320: Na salt, Shore D hardness 37, M.I. 1.1 g/10 min. (190° C.)
S9320: Zn salt, Shore D hardness 36, M.I. 1.0 g/10 min. (190° C.)
*3 thermoplastic elastomer having crystalline polyethylene block by Nihon Synthetic Rubber K.K.
DYNARON E6100P: hydrogenated polybutadiene, M.I. 0.6 g/10 min. (230° C.), styrene content 0%, E-EB-E type
DYNARON E4600P: hydrogenated butadiene-styrene copolymer, M.I. 5.6 g/10 min. (230° C.), styrene content 20%, E-EB-E type
*4 ionomer resins by Mitsui dupont Polychemical K.K.
H1706: Zn salt, Shore D hardness 62, M.I. 0.9 g/10 min. (190° C.)
H1605: Na salt, Shore D hardness 63, M.I. 2.8 g/10 min. (190° C.)
H1855: Zn salt, Shore D hardness 56, M.I. 1.0 g/10 min. (190° C.)
H1557: Zn salt, Shore D hardness 60, M.I. 5.0 g/10 min. (190° C.)
H1601: Na salt, Shore D hardness 62, M.I. 1.2 g/10 min. (190° C.)

It is evident from Tables 2 and 3 that the two-piece golf balls of Comparative Examples 1 and 2 are less durable against hitting. Of the golf balls of Comparative Examples 3 to 6 having an intermediate layer composed of a blend of ionomer resins, Comparative Examples 3 to 5 travel a short distance and Comparative Example 6 is poor in feel and durability. In Comparative Example 7, the intermediate layer shows molding defects because the blend contains an ionomer resin having a low melt index.

In contrast, the golf balls of Examples 1 to 9 are improved in all of the moldability of the intermediate layer, flight performance, hitting feel and durability against hitting.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A golf ball comprising a core, an intermediate layer enclosing the core, and a cover enclosing the intermediate layer,

said intermediate layer comprising a resin component based on a mixture of 10 to 60 parts by weight of a thermoplastic elastomer having a crystalline polyethylene block and 90 to 40 parts by weight of an ionomer resin having a melt index of at least 3 g/10 min. at 190° C.

2. The golf ball of claim 1 wherein said thermoplastic elastomer having a crystalline polyethylene block is a thermoplastic elastomer having a polyethylene block or a polyethylene block and a polystyrene block as a hard segment and an ethylene/butylene random copolymer as a soft segment.

3. The golf ball of claim 1 wherein said thermoplastic elastomer comprises a hydrogenated product of polybutadiene or styrene/butadiene copolymer.

4. The golf ball of claim 1 wherein said thermoplastic elastomer has a melt index of 0.01 to 15 g/10 min. at 230° C. and a surface hardness of 10 to 50 in Shore D.

5. The golf ball of claim 1 wherein said ionomer resin is a mixture of an ionomer resin having a monovalent metal and an ionomer resin having a divalent metal and has a Shore D hardness of 60 to 70.

6. The golf ball of claim 1 wherein said intermediate layer has a Shore D hardness of 48 to 62.

7. The golf ball of claim 1 which has a distortion of 2.5 to 4 mm under a constant load of 100 kg.

8. The golf ball of claim 1 wherein said cover is mainly formed of an ionomer resin and has a Shore D hardness of 50 to 68.

9. The golf ball of claim 1, wherein said thermoplastic elastomer has a melt index of 0.03 to 10 g/10 min. at 230° C.

10. The golf ball of claim 1, wherein said intermediate layer has a Shore D hardness of 50 to 58.

11. The golf ball of claim 1, wherein said intermediate layer has a thickness in the range of 1.2 to 2.5 mm and a specific gravity in the range of 0.9 to 1.3.

12. The golf ball of claim 1, wherein said core is a solid core having a distortion in the range of 2.8 to 4.5 mm under a constant load of 100 kg.

13. The golf ball of claim 1, wherein said core is a solid core having a diameter in the range of 34.3 to 38.7 mm and a weight in the range of 28.5 to 35 grams.

14. The golf ball of claim 1, wherein said cover has a surface hardness in the range of 54 to 60 on Shore D.

15. The golf ball of claim 1, wherein said cover has a thickness in the range of 1 to 3 mm.

16. The golf ball of claim 1, wherein a total thickness of said intermediate layer and said cover is in the range of 2.0 to 4.2 mm.

17. The golf ball of claim 1, wherein said golf ball has a distortion of 2.8 to 3.5 mm under a constant load of 100 kg.

* * * * *

Exhibit E

US006267694B1

(12) United States Patent

Higuchi et al.

(10) Patent No.: US 6,267,694 B1

(45) Date of Patent: *Jul. 31, 2001

(54) MULTI-PIECE SOLID GOLF BALL

(75) Inventors: Hiroshi Higuchi; Yasushi Ichikawa; Hisashi Yamagishi; Junji Hayashi; Akira Kawata, all of Chichibu (JP)

(73) Assignee: Bridgestone Sports Co., Ltd., Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: 09/131,772

(22) Filed: Aug. 10, 1998

Related U.S. Application Data

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(30) **Foreign Application Priority Data**

Aug. 8, 1997 (JP) 9-227609
Oct. 22, 1997 (JP) 9-307971

(51) Int. Cl.[7] A63B 37/06
(52) U.S. Cl. 473/374; 473/373
(58) Field of Search 473/373, 378, 473/351, 374, 377

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(74) *Attorney, Agent, or Firm*—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC

(57) **ABSTRACT**

A multi-piece solid golf ball featuring an increased flight distance, superior control, good feeling, and improved durability is provided. A multi-piece solid golf ball comprising a solid core and a cover of two inner and outer layers surrounding the core is characterized in that the solid core has a distortion of at least 2.4 mm under an applied load of 100 kg, the inner cover layer is formed mainly of an ionomer resin to a Shore D hardness of 28–58, and the outer cover layer is formed mainly of a thermoplastic polyurethane elastomer to a Shore D hardness of 30–55.

17 Claims, 1 Drawing Sheet

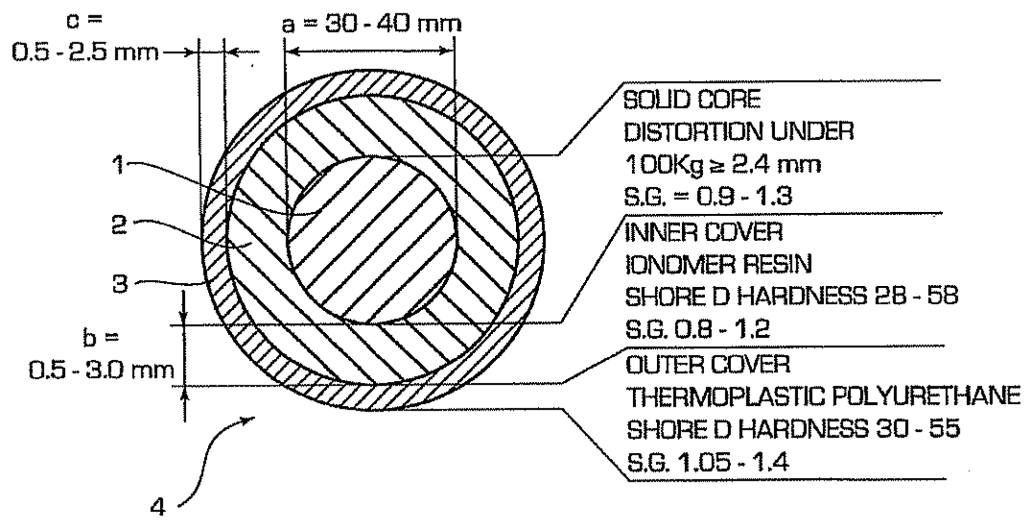
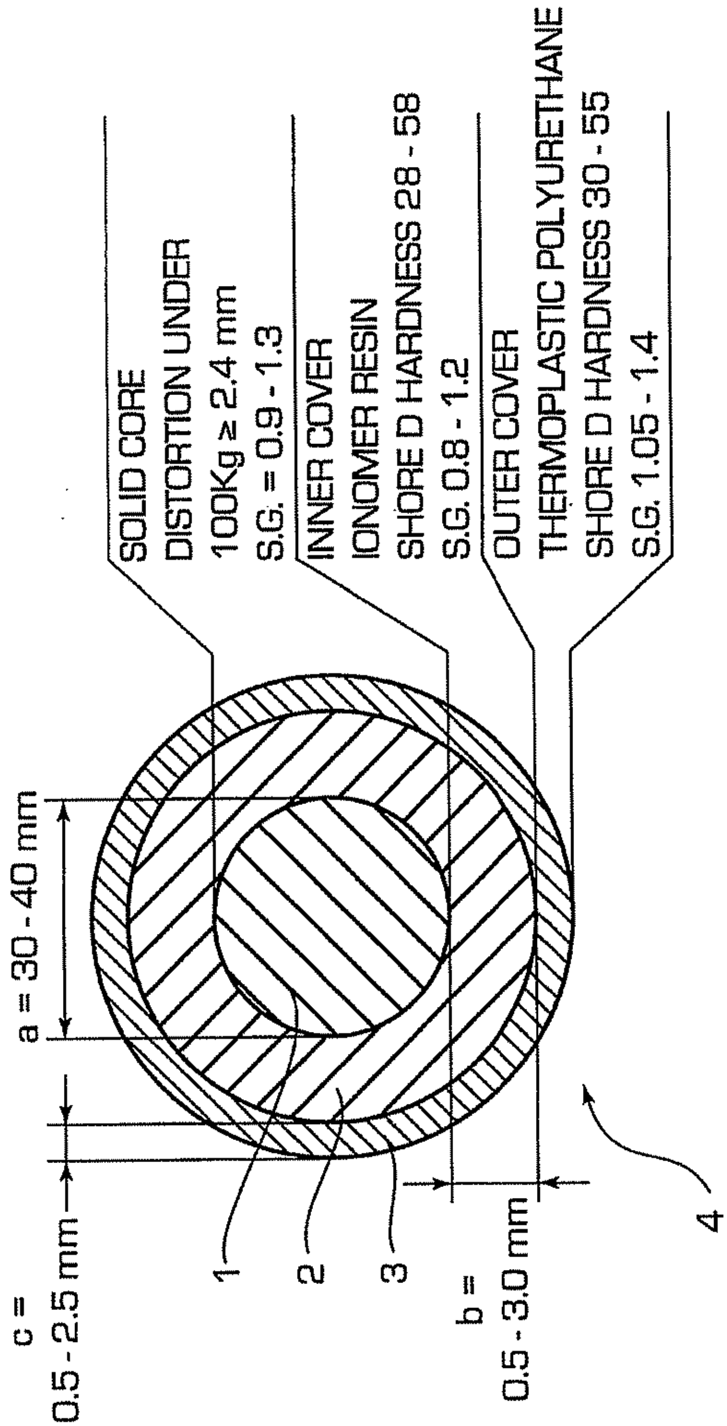


FIG. 1


SOLID CORE
DISTORTION UNDER
100Kg ≥ 2.4 mm
S.G. = 0.9 - 1.3
INNER COVER
IONOMER RESIN
SHORE D HARDNESS 28 - 58
S.G. 0.8 - 1.2
OUTER COVER
THERMOPLASTIC POLYURETHANE
SHORE D HARDNESS 30 - 55
S.G. 1.05 - 1.4
a = 30 - 40 mm
c = 0.5 - 2.5 mm
b = 0.5 - 3.0 mm
1
2
3
4

MULTI-PIECE SOLID GOLF BALL

CROSS REFERENCE TO RELATED APPLICATION

This application is an application filed under 35 U.S.C.§111(a) claiming benefit pursuant to 35 U.S.C. § 119(e)(i) of the filing date of the Provincial Application 60/058,564 filed on September 11, 1997 pursuant to 35 U.S.C. §111(b).

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a multi-piece solid golf ball comprising a solid core enclosed with a cover of two inner and outer layers.

2. Prior Art

Golf balls of various structures have recently been proposed. In particular, many proposals were made on solid golf balls, inter alia, multi-piece solid golf balls comprising a solid core enclosed with a cover of plural layers from the standpoints of flight distance, control (or spin rate), and feeling (see JP-A 244174/1992, 142228/1994, 24084/1995, 24085/1995, and 10358/1997).

Nevertheless, there is a desire to have a multi-piece solid golf ball having further improved flight performance, superior spin property, and good feeling upon wood, iron and putter shots as well as good scraping resistance and durability.

SUMMARY OF THE INVENTION

Making extensive investigations to meet the above desire, the inventors have found that it is effective for a multi-piece solid golf ball comprising a solid core and a cover of two layers, an inner and outer layer surrounding the core that the solid core is formed relatively soft, the inner cover layer is formed mainly of an ionomer resin, the outer cover layer is formed mainly of a thermoplastic polyurethane elastomer, the inner cover layer has a Shore D hardness of 28 to 58, and the outer cover layer has a Shore D hardness of 30 to 55.

Specifically, the present invention provides:

(1) A multi-piece solid golf ball comprising a solid core and a cover of two inner and outer layers surrounding the core, characterized in that said solid core has a distortion of at least 2.4 mm under an applied load of 100 kg, said inner cover layer is formed mainly of an ionomer resin to a Shore D hardness of 28 to 58, and said outer cover layer is formed mainly of a thermoplastic polyurethane elastomer to a Shore D hardness of 30 to 55.

(2) The golf ball of (1) wherein the resin of said inner cover layer is a mixture of an ionomer resin and an olefinic elastomer in a weight ratio between 40:60 and 95:5.

(3) The golf ball of (1) or (2) wherein in said outer cover layer, an ionomer resin having a Shore D hardness of at least 55 is mixed in a proportion of less than 70 parts by weight per 100 parts by weight of the thermoplastic polyurethane elastomer.

(4) The golf ball of any one of (1) to (3) wherein the ball as a whole has an inertia moment of at least 83 g-cm^2.

(5) The golf ball of any one of (1) to (4) wherein 1 to 30% by weight of an inorganic filler is added to said outer cover layer.

(6) The golf ball of any one of (1) to (5) wherein 1 to 30% by weight of an inorganic filler is added to said inner cover layer.

(7) The golf ball of any one of (1) to (6) wherein said outer cover layer has a specific gravity of 1.05 to 1.4.

(8) The golf ball of any one of (1) to (7) wherein said inner cover layer has a specific gravity of 0.8 to 1.2.

(9) The golf ball of any one of (1) to (8) wherein said core has a specific gravity of 0.9 to 1.3.

(10) The golf ball of any one of (1) to (9) wherein said outer cover layer has a gage of 0.5 to 2.5 mm, said inner cover layer has a gage of 0.5 to 3.0 mm, and said cover has a total gage of 1.0 to 5.5 mm.

The golf ball of the invention features an increased flight distance, superior control upon iron shots, good feeling upon shots with any club of wood, iron and putter, high resistance to scraping upon control shots with an iron, and good durability.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic cross-section of the multi-piece golf ball according to this invention.

DETAILED DESCRIPTION OF THE INVENTION

Now the invention is described in more detail.

The multi-piece solid golf ball of the invention has a solid core 1 and a cover 4 surrounding the core of a two-layer structure of inner and outer cover layers 2 and 3.

The solid core 1 used herein is formed mainly of a rubber base. Natural rubber and/or synthetic rubber which is used in conventional solid golf balls can be used as the rubber base although 1,4-polybutadiene having at least 40% of a cis structure is especially preferred in the practice of the invention. Herein, natural rubber, polyisoprene rubber, styrene-butadiene rubber or the like may be blended with the polybutadiene rubber if desired.

More particularly, the solid core 1 of the golf ball according to the invention is obtained in conventional ways by adjusting vulcanizing conditions and blending ratio. In general, the solid core composition contains a base rubber, a crosslinking agent, a co-crosslinking agent, an inert filler, etc. The base rubber used may be the above-mentioned natural rubber and/or synthetic rubber. The crosslinking agent is exemplified by organic peroxides such as dicumyl peroxide and di-t-butyl peroxide, with the dicumyl peroxide being especially preferred. The amount of the crosslinking agent blended is usually 0.5 to 2.0 parts by weight per 100 parts by weight of the base rubber.

The co-crosslinking agent is not critical and exemplified by metal salts of unsaturated fatty acids, especially zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms (e.g., acrylic acid and methacrylic acid), with zinc acrylate being especially preferred. The amount of the co-crosslinking agent blended is 10 to 50 parts by weight, preferably 20 to 48 parts by weight per 100 parts by weight of the base rubber.

Examples of the inert filler include zinc oxide, barium sulfate, silica, calcium carbonate, and zinc carbonate, with zinc oxide and barium sulfate being commonly used. The amount of the filler blended is governed by the specific gravity of the core and the cover, the weight specification of the ball, etc. and not critical although it is usually 3 to 30 parts by weight per 100 parts by weight of the base rubber. It is understood that in the practice of the invention, the solid core is given an optimum hardness by properly adjusting the amount of zinc oxide and barium sulfate blended.

A solid core composition is prepared by kneading the above-mentioned components in a conventional mixer such

as a Banbury mixer and roll mill, and it is compression or injection molded in a core mold. The molding is then cured into a solid core by heating at a sufficient temperature for the crosslinking agent and co-crosslinking agent to function (for example, about 130 to 170° C. when dicumyl peroxide and zinc acrylate are used as the crosslinking agent and the co-crosslinking agent, respectively).

The solid core 1 should have a distortion or deformation of at least 2.4 mm, preferably 2.7 to 7.0 mm, more preferably 2.9 to 5.5 mm under an applied load of 100 kg. A distortion of less than 2.4 mm under an applied load of 100 kg (hard core) would give disadvantages such as a hard hitting feel. A too much distortion (too soft core) would sometimes fail to provide sufficient restitution.

The solid core 1 preferably has a specific gravity of 0.9 to 1.3, especially 1.0 to 1.25.

In the practice of the invention, the solid core 1 preferably has a diameter (2) of 30 to 40 mm, especially 33 to 39 mm. Also the solid core may be of multi-layer structure insofar as it satisfies the above-defined distortion under an applied load of 100 kg.

Next, the inner cover layer 2 is formed mainly of an ionomer resin. The ionomer resin may be used alone or in admixture of two or more and is selected on use so as to satisfy the Shore D hardness and specific gravity described below. For example, "Surlyn" by E. I. duPont, "Himilan" by Mitsui duPont Polychemicals K. K., and "Iotek" by Exxon may be used.

In this regard, by mixing the ionomer resin with an olefinic elastomer, properties (e.g., hitting feel and restitution) which are not available when they are used alone can be obtained. The olefinic elastomer used herein includes linear low-density polyethylene, low-density polyethylene, high-density polyethylene, polypropylene, rubber-reinforced olefin polymers, flexomers, plastomers, thermoplastic elastomers (styrene block copolymers and hydrogenated polybutadiene-ethylene-propylene rubber) including acid-modified products, dynamically vulcanized elastomers, ethylene acrylate, and ethylene-vinyl acetate. For example, "HPR" by Mitsui duPont Polychemicals K.K. and "Dynalon" by Nippon Synthetic Rubber K.K. are used.

The mixing proportion of the ionomer resin to the olefinic elastomer is desirably between 40:60 and 95:5, preferably between 45:55 and 90:10, more preferably between 48:52 and 88:12, especially between 55:45 and 85:15 in weight ratio. Too less contents of the olefinic elastomer would lead to hard hitting feel. On the other hand, too large contents of the olefinic elastomer would detract from resiliency.

Understandably, another polymer may be blended with the ionomer resin insofar as the benefits of the invention are not impaired.

Further the inner cover layer 2 composed mainly of the ionomer resin may contain about 30% by weight or less of an inorganic filler such as zinc oxide, barium sulfate, and titanium dioxide. Preferably the amount of the filler is 1 to 30% by weight.

The inner cover layer 2 should have a Shore D hardness of 28 to 58, especially 30 to 57. A Shore D hardness of less than 28 would detract from restitution whereas hitting feel would be exacerbated above 58.

Further, the inner cover layer 2 should preferably have a specific gravity of 0.8 to 1.2, especially 0.9 to 1.18.

It is noted that the inner cover layer preferably has a gage (6) of 0.5 to 3.0 mm, especially 0.9 to 2.5 mm.

On the other hand, the outer cover layer 3 is formed of a thermoplastic polyurethane elastomer.

The thermoplastic polyurethane elastomer used herein has a molecular structure consisting of a high molecular weight polyol compound constituting a soft segment, a monomolecular chain extender constituting a hard segment, and a diisocyanate.

The high molecular weight polyol compound is not critical and may be any of polyester polyols, polyether polyols, copolyester polyols, and polycarbonate polyols. Exemplary polyester polyols include polycaprolactone glycol, poly (ethylene-1,4-adipate) glycol, and poly(butylene-1,4-adipate) glycol; an exemplary copolyester polyol is poly (diethylene glycol adipate) glycol; an exemplary polycarbonate polyol is (hexanediol-1,6-carbonate) glycol; and an exemplary polyether polyol is polyoxytetramethylene glycol. Their number average molecular weight is about 600 to 5,000, preferably 1,000 to 3,000.

As the diisocyanate, aliphatic diisocyanates are preferably used in consideration of the yellowing resistance of the cover. Examples include hexamethylene diisocyanate (HDI), 2,2,4- or 2,4,4-trimethylhexamethylene diisocyanate (TMDI), and lysine diisocyanate (LDI). HDI is especially preferred for its compatibility with another resin upon blending.

The monomolecular chain extender is not critical and may be selected from conventional polyhydric alcohols and amines. Examples include 1,4-butylene glycol, 1,2-ethylene glycol, 1,3-propylene glycol, 1,6-hexylene glycol, 1,3-butylene glycol, dicyclohexylmethylmethanediamine (hydrogenated MDA), and isophoronediamine (IPDA).

Of the thermoplastic polyurethane elastomers, those having a tanδ peak temperature of lower than −15° C., especially −16° C. to −50° C. as determined by viscoelasticity measurement are preferred in view of softness and resiliency.

As the thermoplastic polyurethane elastomer, there may be used commercially available ones whose diisocyanate component is aliphatic, for example, Pandex T7298 (−20° C.), T7295 (−26° C.), and T7890 (−30° C.) (by Dai-Nihon Ink Chemical Industry K.K.). Note that the numerals in parentheses each represent a tanδ peak temperature.

To the thermoplastic polyurethane elastomer, if necessary, an ionomer resin having a Shore D hardness of at least 55, preferably 55 to 70, more preferably 56 to 69 can be added in an amount of 0 to 70 parts by weight, especially 0 to 35 parts by weight per 100 parts by weight of the thermoplastic polyurethane elastomer. Resiliency can be improved by blending the ionomer resin. When the ionomer resin is blended, its lower limit is 1 part by weight.

Further the outer cover layer 3 composed mainly of the thermoplastic polyurethane elastomer may contain 1 to 30% by weight, especially 1.5 to 28% by weight of an inorganic filler such as zinc oxide, barium sulfate, and titanium dioxide.

The outer cover layer 3 should have a Shore D hardness of 30 to 55, preferably 32 to 54, more preferably 33 to 53. A Shore D hardness of less than 30 would lead to low restitution whereas hitting feel would be exacerbated above 55.

The outer cover layer 3 should preferably have a specific gravity of 1.05 to 1.4, especially 1.1 to 1.35.

The outer cover layer preferably has a gage (6) of 0.5 to 2.5 mm, especially 1.0 to 2.3 mm.

In this regard, the inner and outer cover layers 2 and 3 preferably have a total gage (overall cover gage) of 1.0 to 5.5 mm, especially 1.5 to 5.3 mm.

Understandably, the inner and outer cover layers may be formed by well-known techniques such as injection molding and compression molding using half shells.

The multi-piece solid golf ball thus obtained should preferably have an inertia moment of at least 83 g-cm^2, especially 83 to 90 g-cm^2 as measured by the method described later. An inertia moment of less than 83 g-cm^2 would lead to the disadvantage that the ball rolling upon putting becomes unsustained.

The outer cover layer **3** is formed with dimples in a conventional manner. With respect to the diameter, weight and other parameters, the golf ball of the invention is constructed in accordance with the Rules of Golf to a diameter of not less than 42.67 mm and a weight of not greater than 45.93 grams.

There has been described a multi-piece solid golf ball featuring an increased flight distance, superior control, pleasant feeling, and improved durability.

EXAMPLE

Examples of the present invention are given below together with Comparative Examples by way of illustration and not by way of limitation.

Examples and Comparative Examples

Solid cores of the composition shown in Table 1 were prepared.

TABLE 1

Solid core	Example					Comparative Example					
composition (pbw)	1	2	3	4	5	1	2	3	4	5	6
Polybutadiene*	100	100	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Barium sulfate	12.5	7	15.5	8.5	7.8	0	19	21.2	12.9	20.7	10
Zinc oxide	5	5	5	5	5	3.8	5	5	5	5	5
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zinc salt of pentachlorothiophenol	1	1	1	1	1	1	1	1	1	1	1
Zinc acrylate	29.6	25.9	23.7	29.6	25.9	39.2	33.3	25.9	34	34	31.8

*Polybutadiene: BR01 by Nippon Synthetic Rubber K.K.

Next, the cores each were enclosed with an inner cover layer of the composition shown in Table 2 by injection molding and then with an outer cover layer of the composition shown in Table 3 by injection molding, obtaining three-piece golf balls having a weight and diameter as shown in Tables 4 and 5.

The golf balls were examined for inertia moment, flight distance, spin rate, feeling, scraping resistance, and consecutive durability by the following tests. The results are shown in Tables 4 and 5.

Inertia moment

It is calculated according to the equation shown below. More particularly, the inertia moment is a value calculated from the diameters (gages) and specific gravities of the respective layers and it can be determined from the following equation on the assumption that the ball is spherical. Although the ball is regarded spherical for the calculation purpose, the specific gravity of the outer cover layer is lower than the specific gravity of the outer cover-forming resin itself because the dimples are present on the actual ball. The specific gravity of the outer cover layer is herein designated a phantom outer cover layer specific gravity, which is used for the calculation of an inertia moment M.

$$M=(/5880000)x\{(r1-r2)xD1^5+(r2-r3)xD2^5+r3xD3^5\}$$

M: inertia moment (g-cm^2)

r1: core specific gravity

D1: core diameter

r2: inner cover layer specific gravity

D2: inner cover layer diameter (the diameter of a sphere obtained by forming the inner cover layer around the core)

r3: phantom outer cover layer specific gravity

D3: outer cover layer diameter (ball diameter)

Note that the diameters are expressed in mm.

Flight distance

Using a swing robot, the ball was hit with a driver (#W1, head speed 45 m/sec.) to measure a carry and total distance.

Spin rate

A spin rate was calculated from photographic analysis by photographing the behavior of the ball immediately after impact with #W1 and a sand wedge (#SW, head speed 20 m/sec.).

Feeling

Three professional golfers actually hit the ball with #W1 and a putter (#PT) to examine the ball for feeling according to the following criteria.

O: soft

: somewhat hard

X: hard

Scraping resistance

Using the swing robot, the ball was hit at arbitrary two points with a sand wedge (#SW, head speed 38 m/sec.). The ball at the hit points was visually examined.

O: good

: medium

X: poor

Consecutive durability

Using a flywheel hitting machine, the ball was repeatedly hit at a head speed of 38 m/sec. The ball was evaluated in terms of the number of hits repeated until the ball was broken.

O: good

X: poor

TABLE 2

Inner cover layer (pbw)	Shore D	Specific gravity	a	b	c	d	e	f	g	h
HPR AR201	about 5	0.96	—	—	20	40	—	—	—	
Dynalon 6100P	35	0.88	48	30	—	—	—	—	—	—
Hytrel 4047	40	1.12	—	—	—	—	100	—	—	—
PEBAX 3533	42	1.01	—	—	—	—	—	100	—	
Surlyn AD8511	63	0.94	26	35	40	30	—	—	—	—
Surlyn AD8512	63	0.94	26	35	40	30	—	—	—	—
Himilan 1605	61	0.94	—	—	—	—	—	—	—	50
Himilan 1706	60	0.94	—	—	—	—	—	—	60	50
Surlyn 8120	45	0.94	—	—	—	—	—	—	40	—
Titanium dioxide	—	4.2	5.1	25	5.1	5.1	0	0	5.1	5.1

HPR AR201: Mitsui duPont Polychemicals K.K., acid-modified thermo-plastic resin

Dynalon: Nippon Synthetic Rubber K.K., block copolymer, hydrogenated butadiene-styrene copolymer

Hytrel: Toray duPont K.K., thermoplastic polyester elastomer

PEBAX: Atochem, polyamide elastomer

Surlyn: E. I. dupont, ionomer resin

Himilan: Mitsui duPont Polychemicals K.K., ionomer resin

TABLE 3

Outer cover layer (pbw)	Shore D	Specific gravity	A	B	C	D	E	F	G
PANDEX T7890	39	1.16	—	100	80	—	—	—	—
PANDEX T7298	50	1.16	100	—	—	—	—	—	—
Himilan 1605	61	0.94	—	—	10	—	50	—	—
Himilan 1706	60	0.94	—	—	10	—	50	40	70
Surlyn 8120	45	0.94	—	—	—	100	—	60	30
Titanium dioxide	—	4.2	2.7	2.7	25	5.13	5.13	5.13	5.13

PANDEX: Dai-Nihon Ink Chemical Industry K.K., thermoplastic polyurethane elastomer
Himilan: Mitsui dupont Polychemicals K.K., ionomer resin
Surlyn: E. I. duPont, ionomer resin

TABLE 4

		Example				
		1	2	3	4	5
Solid core	Weight (g)	29.63	28.11	27.76	28.36	28.46
	Diameter (mm)	36.60	36.40	35.80	36.30	36.50
	Distortion @ 100 kg (mm)	3.50	4.00	4.30	3.50	4.00
	Specific gravity	1.154	1.113	1.156	1.132	1.118
Inner cover layer	Type	a	b	c	d	a
	Shore D hardness	51	56	53	41	51
	Specific gravity	0.95	1.09	0.98	0.98	0.95
	Gage (mm)	1.60	1.70	2.00	1.20	1.60
Outer cover layer	Type	A	A	B	A	C
	Specific gravity	1.183	1.183	1.183	1.183	1.299
	Gage (mm)	1.45	1.45	1.45	2.00	1.50
	Shore D hardness	50	50	39	50	44
Ball	Weight (g)	45.30	45.30	45.30	45.30	45.30
	Diameter (mm)	42.70	42.70	42.70	42.70	42.70
Inertia moment ($g\text{-}cm^2$)		83.1	84.3	83.1	83.8	84.5
#W1/HS45	Carry (m)	209.0	208.6	208.6	208.8	208.6
	Total (m)	223.8	223.9	222.9	223.2	222.8
	Spin (rpm)	2771	2668	2846	2851	2802
	Feeling	○	○	○	○	○
#SW/HS20 approach spin (rpm)		6188	6125	6318	6215	6281
#PT feeling		○	○	○	○	○
Scraping resistance		○	○	○	○	○
Consecutive durability		○	○	○	○	○

TABLE 5

		Comparative Example					
		1	2	3	4	5	6
Solid core	Weight (g)	25.83	30.25	27.47	29.72	30.76	29.16
	Diameter (mm)	35.50	36.40	35.30	36.50	36.50	36.50
	Distortion @ 100 kg (mm)	2.20	3.00	4.00	2.90	2.90	3.20
	Specific gravity	1.103	1.198	1.193	1.167	1.208	1.145
Inner cover layer	Type	e	f	e	e	g	h
	Shore D hardness	40	42	40	40	56	62
	Specific gravity	1.12	1.01	1.12	1.12	0.98	0.98
	Gage (mm)	11.63	1.80	1.70	1.60	1.60	1.60
Outer cover layer	Type	A	D	E	F	G	A
	Specific gravity	1.183	0.980	0.980	0.980	0.980	1.183
	Gage (mm)	1.98	1.35	2.00	1.50	1.50	1.50
	Shore D hardness	50	45	62	53	58	50
Ball	Weight (g)	45.30	45.30	45.30	45.30	45.30	45.30
	Diameter (mm)	42.70	42.70	42.70	42.70	42.70	42.70
Inertia moment (g-cm^2)		84.6	81.2	81.3	82.1	80.9	83.4
#W1/HS45	Carry (m)	208.1	205.3	207.9	205.8	207.9	208.1
	Total (m)	217.2	217.5	221.0	218.1	219.2	220.3
	Spin (rpm)	3075	3001	2548	2898	2689	2734
	Feeling	X		O		O	O
#SW/HS20 approach spin (rpm)		6251	6236	4923	6211	5632	6132
#PT feeling		O	O	X	O	X	X
Scraping resistance		O		O			X
Consecutive durability		O	O	X	O	O	X

What is claimed:

1. A multi-piece solid golf ball comprising: a solid core and a cover consisting of inner and outer layers surrounding the core, characterized in that said solid core has a distortion of at least 2.4 mm under an applied load of 100 kg, said inner cover layer consisting essentially of an ionomer resin to a Shore D hardness of 28 to 58, and said outer cover layer consisting essentially of a thermoplastic polyurethane elastomer to a Shore D hardness of 30 to 55.

2. The golf ball of claim 1 wherein the resin of said inner cover layer is a mixture of an ionomer resin and an olefinic elastomer in a weight ratio between 40:60 and 95:5.

3. The golf ball of claim 1 wherein in said outer cover layer, an ionomer resin having a Shore D hardness of at least 55 is mixed in a proportion of less than 70 parts by weight per 100 parts by weight of the thermoplastic polyurethane elastomer.

4. The golf ball of claim 1 wherein the ball as a whole has an inertia moment of at least 83 g-cm^2.

5. The golf ball of claim 1 wherein 1 to 30% by weight of an inorganic filler is added to said outer cover layer.

6. The golf ball of claim 1 wherein 1 to 30% by weight of an inorganic filler is added to said inner cover layer.

7. The golf ball of claim 1 wherein said outer cover layer has a specific gravity of 1.05 to 1.4.

8. The golf ball of claim 1 wherein said inner cover layer has a specific gravity of 0.8 to 1.2.

9. The golf ball of claim 1 wherein said core has a specific gravity of 0.9 to 1.3.

10. The golf ball of claim 1 wherein said outer cover layer has a gage of 0.5 to 2.5 mm, said inner cover layer has a gage of 0.5 to 3.0 mm, and said cover has a total gage of 1.0 to 5.5 mm.

11. The golf ball of claim 1 wherein said inner cover layer has a Shore D hardness in the range 30 to 57.

12. The golf ball of claim 1 wherein said outer cover layer has a Shore D hardness in the range 33 to 53.

13. The golf ball of claim 1 wherein said outer cover layer consists essentially of a thermoplastic polyurethane elastomer containing less than 30% by weight of an inorganic filler.

14. The golf ball of claim 1 wherein said inner cover layer consists essentially of an ionomer resin containing less than 30% by weight of an inorganic filler.

15. The golf ball of claim 1, wherein said core has a distortion of 2.7 to 7.0 mm under an applied load of 100 kg.

16. The golf ball of claim 1, wherein said inner core has a distortion of 2.9 to 5.5 mm under an applied load of 100 kg.

17. The golf ball of claim 1, wherein said cover layer is a mixture of an ionomer resin and an olefinic elastomer in a weight ratio between 55:45 and 85:15.

* * * * *

Exhibit F

US006174247B1

(12) **United States Patent**
Higuchi et al.

(10) **Patent No.: US 6,174,247 B1**
(45) **Date of Patent: *Jan. 16, 2001**

(54) **MULTI-PIECE SOLID GOLF BALL**

(75) Inventors: **Hiroshi Higuchi; Yasushi Ichikawa; Hisashi Yamagishi; Junji Hayashi; Akira Kawata**, all of Chichibu (JP)

(73) Assignee: **Bridgestone Sports Co., Ltd.**, Tokyo (JP)

(*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/131,887**

(22) Filed: **Aug. 10, 1998**

Related U.S. Application Data

(60) Provisional application No. 60/058,562, filed on Sep. 11, 1997.

(30) **Foreign Application Priority Data**

Aug. 8, 1997 (JP) 9-227610
Oct. 22, 1997 (JP) 9-307972

(51) **Int. Cl.**[7] **A63B 37/12**
(52) **U.S. Cl.** **473/374**
(58) **Field of Search** 473/373, 374, 473/378, 370, 375, 376

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(74) *Attorney, Agent, or Firm*—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC

(57) **ABSTRACT**

A multi-piece solid golf ball comprises a solid core and a cover of two inner and outer layers surrounding the core. The solid core has a distortion of at least 2.4 mm under an applied load of 100 kg. The inner cover layer is formed mainly of an ionomer resin to a Shore D hardness of 28–58, and the outer cover layer is formed mainly of a thermoplastic polyester elastomer to a Shore D hardness of 28–55.

12 Claims, 1 Drawing Sheet

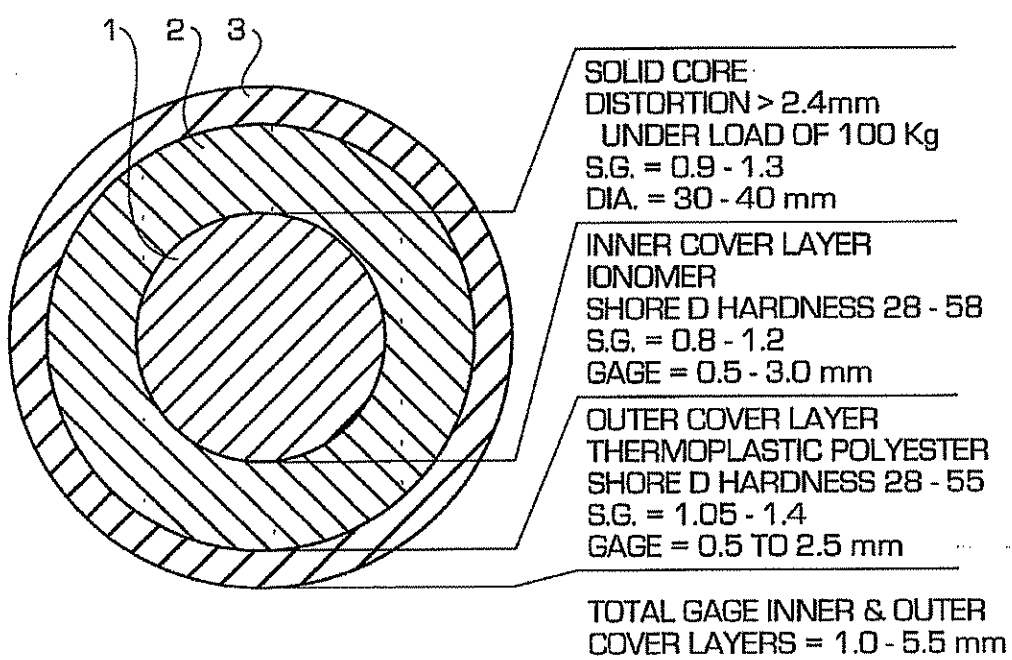
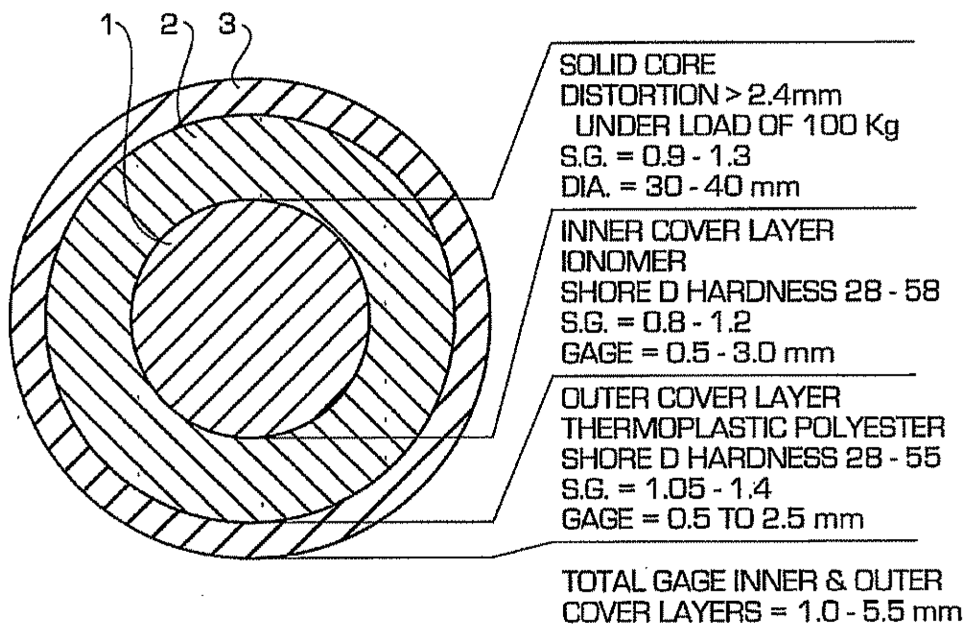


FIG. 1


1
2
3
SOLID CORE
DISTORTION > 2.4mm
UNDER LOAD OF 100 Kg
S.G. = 0.9 - 1.3
DIA. = 30 - 40 mm
INNER COVER LAYER
IONOMER
SHORE D HARDNESS 28 - 58
S.G. = 0.8 - 1.2
GAGE = 0.5 - 3.0 mm
OUTER COVER LAYER
THERMOPLASTIC POLYESTER
SHORE D HARDNESS 28 - 55
S.G. = 1.05 - 1.4
GAGE = 0.5 TO 2.5 mm
TOTAL GAGE INNER & OUTER
COVER LAYERS = 1.0 - 5.5 mm

MULTI-PIECE SOLID GOLF BALL

CROSS REFERRENCE TO RELATED APPLICATION

This application is an application files under 35 U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C. §119(e)(i) of the filing date of the Provincial Application No. 60/058,562 filed on Sep. 11, 1997 pursuant to 35 U.S.C. §111(b).

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a multi-piece solid golf ball comprising a solid core enclosed with a cover of two inner and outer layers.

2. Prior Art

Golf balls of various structures have recently been proposed. In particular, many proposals were made on solid golf balls, inter alia, multi-piece solid golf balls comprising a solid core enclosed with a cover of plural layers from the standpoints of flight distance, control (or spin rate), and feeling (see JP-A 244174/1992, 142228/1994, 24084/1995, 24085/1995, and 10358/1997).

Nevertheless, there is a desire to have a multi-piece solid golf ball having further improved flight performance, superior spin property, and good feeling upon wood, iron and putter shots as well as good scraping resistance and durability.

SUMMARY OF THE INVENTION

Making extensive investigations to meet the above desire, the inventors have found that it is effective for a multi-piece solid golf ball comprising a solid core and a cover of two inner and outer layers surrounding the core that the solid core is formed relatively soft, the inner cover layer is formed mainly of an ionomer resin, the outer cover layer is formed mainly of a thermoplastic polyester elastomer, the inner cover layer has a Shore D hardness of 28 to 58, and the outer cover layer has a Shore D hardness of 28 to 55.

Specifically, the present invention provides:

(1) A multi-piece solid golf ball comprising a solid core and a cover of two inner and outer layers surrounding the core, characterized in that said solid core has a distortion of at least 2.4 mm under an applied load of 100 kg, said inner cover layer is formed mainly of an ionomer resin to a Shore D hardness of 28 to 58, and said outer cover layer is formed mainly of a thermoplastic polyester elastomer to a Shore D hardness of 28 to 55.

(2) The golf ball of (1) wherein the resin of said inner cover layer is a mixture of an ionomer resin and an olefinic elastomer in a weight ratio between 40:60 and 95:5.

(3) The golf ball of (1) or (2) wherein in said outer cover layer, an ionomer resin having a Shore D hardness of at least 55 is mixed in a proportion of less than 70 parts by weight per 100 parts by weight of the thermoplastic polyester elastomer.

(4) The golf ball of any one of (1) to (3) wherein the ball as a whole has an inertia moment of at least 82.5 g-cm^2.

(5) The golf ball of any one of (1) to (4) wherein 1 to 30% by weight of an inorganic filler is added to said outer cover layer.

(6) The golf ball of any one of (1) to (5) wherein 1 to 30% by weight of an inorganic filler is added to said inner cover layer.

(7) The golf ball of any one of (1) to (6) wherein said outer cover layer has a specific gravity of 1.05 to 1.4.

(8) The golf ball of any one of (1) to (7) wherein said inner cover layer has a specific gravity of 0.8 to 1.2.

(9) The golf ball of any one of (1) to (8) wherein said core has a specific gravity of 0.9 to 1.3.

(10) The golf ball of any one of (1) to (9) wherein said outer cover layer has a gage of 0.5 to 2.5 mm, said inner cover layer has a gage of 0.5 to 3.0 mm, and said cover has a total gage of 1.0 to 5.5 mm.

The golf ball of the invention features an increased flight distance, superior control upon iron shots, good feeling upon shots with any club of wood, iron and putter, high resistance to scraping upon control shots with an iron, and good durability.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a cross-section of the golf ball of this invention.

DETAILED DESCRIPTION OF THE INVENTION

Now the invention is described in more detail by reference to FIG. 1.

The multi-piece solid golf ball of the invention has a solid core **1** and a cover surrounding the core of a two-layer structure of inner and outer cover layers **2**,**3**.

The solid core **1** used herein is formed mainly of a rubber base. Natural rubber and/or synthetic rubber which is used in conventional solid golf balls can be used as the rubber base although 1,4-polybutadiene having at least 40% of a cis structure is especially preferred in the practice of the invention. Herein, natural rubber, polyisoprene rubber, styrene-butadiene rubber or the like may be blended with the polybutadiene rubber if desired.

More particularly, the solid core **1** of the golf ball according to the invention is obtained in conventional ways by adjusting vulcanizing conditions and blending ratio. In general, the solid core composition contains a base rubber, a crosslinking agent, a co-crosslinking agent, an inert filler, etc. The base rubber used may be the above-mentioned natural rubber and/or synthetic rubber. The crosslinking agent is exemplified by organic peroxides such as dicumyl peroxide and di-t-butyl peroxide, with the dicumyl peroxide being especially preferred. The amount of the crosslinking agent blended is usually 0.5 to 2.0 parts by weight per 100 parts by weight of the base rubber.

The co-crosslinking agent is not critical and exemplified by metal salts of unsaturated fatty acids, especially zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms (e.g., acrylic acid and methacrylic acid), with zinc acrylate being especially preferred. The amount of the co-crosslinking agent blended is 10 to 50 parts by weight, preferably 20 to 48 parts by weight per 100 parts by weight of the base rubber.

Examples of the inert filler include zinc oxide, barium sulfate, silica, calcium carbonate, and zinc carbonate, with zinc oxide and barium sulfate being commonly used. The amount of the filler blended is governed by the specific gravity of the core and the cover, the weight specification of the ball, etc. and not critical although it is usually 3 to 30 parts by weight per 100 parts by weight of the base rubber. It is understood that in the practice of the invention, the solid core is given an optimum hardness by properly adjusting the amount of zinc oxide and barium sulfate blended.

A solid core composition is prepared by kneading the above-mentioned components in a conventional mixer such

as a Banbury mixer and roll mill, and it is compression or injection molded in a core mold. The molding is then cured into a solid core by heating at a sufficient temperature for the crosslinking agent and co-crosslinking agent to function (for example, about 130 to 170° C. when dicumyl peroxide and zinc acrylate are used as the crosslinking agent and the co-crosslinking agent, respectively).

The solid core 1 should have a distortion or deformation of at least 2.4 mm, preferably 2.4 to 7.0 mm, more preferably 2.9 to 6.0 mm under an applied load of 100 kg. A distortion of less than 2.4 mm under an applied load of 100 kg (hard core) would give disadvantages such as a hard hitting feel. A too much distortion (too soft core) would sometimes fail to provide sufficient restitution.

The solid core 1 preferably has a specific gravity of 0.9 to 1.3, especially 1.0 to 1.25.

In the practice of the invention, the solid core 1 preferably has a diameter of 30 to 40 mm, especially 33 to 39 mm. Also the solid core may be of multi-layer structure insofar as it satisfies the above-defined distortion under an applied load of 100 kg.

Next, the inner cover layer 2 is formed mainly of an ionomer resin. The ionomer resin may be used alone or in admixture of two or more and is selected on use so as to satisfy the Shore D hardness and specific gravity described below. For example, "Surlyn" by E. I. duPont and "Himilan" by Mitsui duPont Polychemicals K.K. may be used.

In this regard, by mixing the ionomer resin with an olefinic elastomer, properties (e.g., hitting feel and restitution) which are not available when they are used alone can be obtained. The olefinic elastomer used herein includes linear low-density polyethylene, low-density polyethylene, high-density polyethylene, polypropylene, rubber-reinforced olefin polymers, flexomers, plastomers, thermoplastic elastomers (styrene block copolymers and hydrogenated polybutadiene-ethylene-propylene rubber) including acid-modified products, dynamically vulcanized elastomers, ethylene acrylate, and ethylene-vinyl acetate. For example, "HPR" by Mitsui duPont Polychemicals K.K. and "Dynalon" by Nippon Synthetic Rubber K.K. are used.

The mixing proportion of the ionomer resin to the olefinic elastomer is desirably between 40:60 and 95:5, preferably between 45:55 and 90:10, more preferably between 48:52 and 88:12, especially between 55:45 and 85:15 in weight ratio. Too less contents of the olefinic elastomer would lead to hard hitting feel. On the other hand, too large contents of the olefinic elastomer would detract from resiliency.

Understandably, another polymer may be blended with the ionomer resin insofar as the benefits of the invention are not impaired.

Further the inner cover layer 2 composed mainly of the ionomer resin may contain about 1 to 30% by weight of an inorganic filler such as zinc oxide, barium sulfate, and titanium dioxide.

The inner cover layer 2 should have a Shore D hardness of 28 to 58, especially 30 to 57. A Shore D hardness of less than 28 would detract from restitution whereas hitting feel would be exacerbated above 58.

Further, the inner cover layer 2 should preferably have a specific gravity of 0.8 to 1.2, especially 0.9 to 1.18.

It is noted that the inner cover layer preferably has a gage of 0.5 to 3.0 mm, especially 0.9 to 2.5 mm.

On the other hand, the outer cover layer 3 is formed mainly of a thermoplastic polyester elastomer.

The thermoplastic polyester elastomer used herein includes polyether ester type multi-block copolymers synthesized from terephthalic acid, 1,4-butane diol, and polytetramethylene glycol (PTMG) or polypropylene glycol (PPG) wherein polybutylene terephthalate (PBT) portions become hard segments and polytetramethylene glycol (PTMG) or polypropylene glycol (PPG) portions become soft segments, for example, Hytrel 3078, 4047, G3548W, 4767, and 5577 (by Toray duPont K.K.).

To the thermoplastic polyester elastomer, an ionomer resin having a Shore D hardness of at least 55, preferably 55 to 70, more preferably 56 to 68 can be added in a proportion of 0 to 70 parts by weight per 100 parts by weight of the thermoplastic polyester elastomer. Resiliency can be improved by blending the ionomer resin. When the ionomer resin is blended, its lower limit is 1 part by weight.

Further the outer cover layer 3 composed mainly of the thermoplastic polyester elastomer may contain 1 to about 30% by weight of an inorganic filler such as zinc oxide, barium sulfate, and titanium dioxide.

The outer cover layer 3 should have a Shore D hardness of 28 to 55, preferably 29 to 53, more preferably 30 to 52. A Shore D hardness of less than 28 would lead to low restitution whereas hitting feel would be exacerbated above 55.

The outer cover layer 3 should preferably have a specific gravity of 1.05 to 1.4, especially 1.07 to 1.3.

The outer cover layer 3 preferably has a gage of 0.5 to 2.5 mm, especially 0.9 to 2.3 mm.

In this regard, the inner and outer cover layers 2,3 preferably have a total gage (overall cover gage) of 1.0 to 5.5 mm, especially 1.5 to 5.3 mm.

Understandably, the inner and outer cover layers may be formed by well-known techniques such as injection molding and compression molding using half shells.

The multi-piece solid golf ball thus obtained should preferably have an inertia moment of at least 82.5 g-cm^2, especially 83 to 90 g-cm^2 as measured by the method described later. An inertia moment of less than 82.5 g-cm^2 would lead to the disadvantage that the ball rolling upon putting becomes unsustained.

The outer cover layer 3 is formed with dimples in a conventional manner. With respect to the diameter, weight and other parameters, the golf ball of the invention is constructed in accordance with the Rules of Golf to a diameter of not less than 42.67 mm and a weight of not greater than 45.93 grams.

There has been described a multi-piece solid golf ball featuring an increased flight distance, superior control, pleasant feeling, and improved durability.

EXAMPLE

Examples of the present invention are given below together with Comparative Examples by way of illustration and not by way of limitation.

Examples and Comparative Examples

Solid cores of the composition shown in Table 1 were prepared.

TABLE 1

Solid core	Example					Comparative Example					
composition (pbw)	1	2	3	4	5	1	2	3	4	5	6
Polybutadiene*	100	100	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Barium sulfate	13	6.4	15.2	8	13.2	0	19	21.2	12.9	20.7	10
Zinc oxide	5	5	5	5	5	3.8	5	5	5	5	5
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zinc salt of pentachlorothiophenol	1	1	1	1	1	1	1	1	1	1	1
Zinc acrylate	31.1	29.6	25.9	29.6	25.9	39.2	33.3	25.9	34	34	31.8

*Polybutadiene: BR01 by Nippon Synthetic Rubber K.K.

Next, the cores each were enclosed with an inner cover layer of the composition shown in Table 2 by injection molding and then with an outer cover layer of the composition shown in Table 3 by injection molding, obtaining three-piece golf balls having a weight and diameter as shown in Tables 4 and 5.

The golf balls were examined for inertia moment, flight distance, spin rate, feeling, scraping resistance, and consecutive durability by the following tests. The results are shown in Tables 4 and 5.

Inertia Moment

It is calculated according to the equation shown below. More particularly, the inertia moment is a value calculated from the diameters (gages) and specific gravities of the respective layers and it can be determined from the following equation on the assumption that the ball is spherical. Although the ball is regarded spherical for the calculation purpose, the specific gravity of the outer cover layer is lower than the specific gravity of the outer cover-forming resin itself because the dimples are present on the actual ball. The specific gravity of the outer cover layer is herein designated a phantom outer cover layer specific gravity, which is used for the calculation of an inertia moment M.

$$M=(\pi/5880000)\times\{(r1-r2)\times D1^5+(r2-r3)\times D2^5+r3\times D3^5\}$$

M: inertia moment (g-cm^2)

r1: core specific gravity

D1: core diameter

r2: inner cover layer specific gravity

D2: inner cover layer diameter (the diameter of a sphere obtained by forming the inner cover layer around the core)

r3: phantom outer cover layer specific gravity

D3: outer cover layer diameter (ball diameter)

Note that the diameters are expressed in mm.

Flight Distance

Using a swing robot, the ball was hit with a driver (#W1, head speed 45 m/sec.) to measure a carry and total distance.

Spin Rate

A spin rate was calculated from photographic analysis by photographing the behavior of the ball immediately after impact with #W1 and a sand wedge (#SW, head speed 20 m/sec.).

Feeling

Three professional golfers actually hit the ball with #W1 and a putter (#PT) to examine the ball for feeling according to the following criteria.

O: soft

:Δ somewhat hard

X: hard

Scraping Resistance

Using the swing robot, the ball was hit at arbitrary two points with a sand wedge (#SW, head speed 38 m/sec.). The ball at the hit points was visually examined.

O: good

: Δ medium

X: poor

Consecutive Durability

Using a flywheel hitting machine, the ball was repeatedly hit at a head speed of 38 m/sec. The ball was evaluated in terms of the number of hits repeated until the ball was broken.

O: good

X: poor

TABLE 2

Inner cover layer (pbw)	Shore D	Specific gravity	a	b	c	d	e	f	g	h
HPR AR201	about 5	0.96	—	—	20	40	—	—	—	—
Dynalon 6100P	35	0.88	48	30	—	—	—	—	—	—
Hytrel 4047	40	1.12	—	—	—	—	100	—	—	—
PEBAX 3533	42	1.01	—	—	—	—	—	100	—	—
Surlyn AD8511	63	0.94	26	35	40	30	—	—	—	—
Surlyn AD8512	63	0.94	26	35	40	30	—	—	—	—
Himilan 1605	61	0.94	—	—	—	—	—	—	—	50
Himilan 1706	60	0.94	—	—	—	—	—	—	60	50
Surlyn 8120	45	0.94	—	—	—	—	—	—	40	—
Titanium dioxide	—	4.2	5.1	25	5.1	5.1	0	0	5.1	5.1

HPR AR201: Mitsui duPont Polychemicals K.K., acid-modified thermoplastic resin
Dynalon: Nippon Synthetic Rubber K.K., block copolymer, hydrogenated butadiene-styrene copolymer
Hytrel: Toray duPont K.K., thermoplastic polyester elastomer
PEBAX: Atochem, polyamide elastomer
Surlyn: E. I. duPont, ionomer resin
Himilan: Mitsui duPont Polychemicals K.K., ionomer resin

TABLE 3

Outer cover layer (pbw)	Shore D	Specific gravity	A	B	C	D	E	F	G
Hytrel 3078	30	1.08	—	—	60	—	—	—	—
Hytrel 4047	40	1.12	100	—	—	—	—	—	—

TABLE 3-continued

Outer cover layer (pbw)	Shore D	Specific gravity	A	B	C	D	E	F	G
Hytrel 4767	47	1.15	—	100	—	—	—	—	—
Himilan 1605	61	0.94	—	—	20	—	50	—	—
Himilan 1706	60	0.94	—	—	20	—	50	40	70
Surlyn 8120	45	0.94	—	—	—	100	—	60	30
Titanium dioxide	—	4.2	5.1	5.1	25	5.13	5.13	5.13	5.13

Hytrel: Toray duPont K.K., thermoplastic polyester elastomer
Himilan: Mitsui duPont Polychemicals K.K., ionomer resin
Surlyn: E. I. duPont, ionomer resin

TABLE 4

	Example				
	1	2	3	4	5
Core					
Weight (g)	29.80	28.28	26.72	28.26	29.25
Diameter (mm)	36.60	36.40	35.30	36.30	36.50
Distortion @ 100 kg (mm)	3.30	3.50	4.00	3.50	4.00
Specific gravity	1.161	1.120	1.160	1.129	1.149
Inner cover layer					
Type	a	b	c	d	a
Shore D hardness	51	56	53	41	51
Specific gravity	0.95	1.09	0.98	0.98	0.95
Gage (mm)	1.60	1.70	2.25	1.20	1.60
Outer cover layer					
Type	A	A	B	B	C
Specific gravity	1.161	1.161	1.192	1.192	1.201
Gage (mm)	1.45	1.45	1.45	2.00	1.50
Shore D hardness	40	40	47	47	44
Ball					
Weight (g)	45.30	45.30	45.30	45.30	45.30
Diameter (mm)	42.70	42.70	42.70	42.70	42.70
Inertia moment (g-cm^2)	82.8	84.0	83.1	83.9	83.3
#W1/HS45					
Carry (m)	208.7	208.6	208.8	208.6	208.6
Total (m)	222.9	223.1	223.5	222.9	222.8
Spin (rpm)	2963	2928	2731	2912	2798
Feeling	○	○	○	○	○
#SW/HS20 approach spin (rpm)	6353	6315	6263	6302	6291
#PT feeling	○	○	○	○	○
Scraping resistance	○	○	○	○	○
Consecutive durability	○	○	○	○	○

TABLE 5

	Comparative Example					
	1	2	3	4	5	6
Core						
Weight (g)	25.83	30.25	27.47	29.72	30.76	29.16
Diameter (mm)	35.50	36.40	35.30	36.50	36.50	36.50
Distortion @ 100 kg (mm)	2.20	3.00	4.00	2.90	2.90	3.20
Specific gravity	1.103	1.198	1.193	1.167	1.208	1.145
Inner cover layer						
Type	e	f	e	e	g	h
Shore D hardness	40	42	40	40	56	62
Specific gravity	1.12	1.01	1.12	1.12	0.98	0.98

TABLE 5-continued

	Comparative Example					
	1	2	3	4	5	6
Gage (mm)	1.63	1.80	1.70	1.60	1.60	1.60
Outer cover layer						
Type	A	D	E	F	G	A
Specific gravity	1.183	0.980	0.980	0.980	0.980	1.183
Gage (mm)	1.98	1.35	2.00	1.50	1.50	1.50
Shore D hardness	50	45	62	53	58	50
Ball						
Weight (g)	45.30	45.30	45.30	45.30	45.30	45.30
Diameter (mm)	42.70	42.70	42.70	42.70	42.70	42.70
Inertia moment (g-cm^2)	84.6	81.2	81.3	82.1	80.9	83.4
#W1/HS45						
Carry (m)	208.1	205.3	207.9	205.8	207.9	208.1
Total (m)	217.2	217.5	221.0	218.1	219.2	220.3
Spin (rpm)	3075	3001	2548	2898	2689	2734
Feeling	X		○		○	○
#SW/HS20 approach spin (rpm)	6251	6236	4923	6211	5632	6132
#PT feeling	○	Δ○	X	Δ○	X	X
Scraping resistance	○	Δ	○	Δ	Δ	X
Consecutive durability	○	○	X	○	○	X

What is claimed is:

1. A multi-piece solid golf ball comprising; a solid core and a cover consisting of inner and outer cover layers surrounding the core, said solid core has a distortion of at least 2.4 mm under an applied load of 100 kg, the inner cover layer comprising a mixture of an ionomer resin and an olefinic elastomer in a weight ratio between 40:60 and 95:5, said inner cover layer has a Shore D hardness of 28 to 58, and the outer cover layer is formed mainly of a thermoplastic polyester elastomer to a Shore D hardness of 28 to 55.

2. The golf ball of claim 1, wherein said solid core has a distortion of 2.9 to 6.0 mm under an applied load of 100 kg, and said inner cover layer has a Shore D hardness of 28 to 56.

3. The golf ball of claim 1, wherein said solid core has a distortion of 2.9 to 6.0 mm under an applied load of 100 kg, and said inner cover layer has a Shore D hardness of 28 to 53.

4. The golf ball of claim 1, wherein the weight ratio of said ionomer resin to said olefinic elastomer is between 55:45 and 85:15.

5. The golf ball of claim 1 wherein in said outer cover layer, an ionomer resin having a Shore D hardness of at least 55 is mixed in a proportion of less than 70 parts by weight per 100 parts by weight of the thermoplastic polyester elastomer.

6. The golf ball of claim 1 wherein the ball as a whole has an inertia moment of at least 82.5 g-cm^2.

7. The golf ball of claims 1 wherein 1 to 30% by weight of an inorganic filler is added to said outer cover layer.

8. The golf ball of claim 1 wherein 1 to 30% by weight of an inorganic filler is added to said inner cover layer.

9. The golf ball of claim 1 wherein said outer cover layer has a specific gravity of 1.05 to 1.4.

10. The golf ball of claim 1 wherein said inner cover layer has a specific gravity of 0.8 to 1.2.

11. The golf ball of claim 1 wherein said core has a specific gravity of 0.9 to 1.3.

12. The golf ball of claim 1 wherein said outer cover layer has a gage of 0.5 to 2.5 mm, said inner cover layer has a gage of 0.5 to 3.0 mm, and said cover has a total gage of 1.0 to 5.5 mm.

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